Dyes and Pigments 84 (2009) 36–53

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

TDDFT-calculations of Vis/NIR absorbing compounds

Jürgen Fabian*

Technische Universität Dresden, Fachbereich Chemie und Lebensmittelchemie, D-01069 Dresden, Germany

ARTICLE INFO

Article history:
Received 17 April 2009
Received in revised form
21 June 2009
Accepted 23 June 2009
Available online 30 June 2009

Dedicated to Prof. Dr. Dr. h.c. mult. Rudolf Zahradník on the occasion of his 80th birthday.

Keywords:
Dyes
Polymethines
Time-dependent density functional theory calculations
Low-energy electronic transitions
Visible and near infrared absorptions

ABSTRACT

To examine the strengths and limitations of the time-dependent density functional theory in calculating the absorption wavelengths of dye, 130, non-radical, radical and biradical coloured organic compounds, including perylenimide, porphyrin, azobenzene, quinone, croconaine, squaraine and push–pull-type colorants, were randomly selected. The first intense electronic transitions were satisfactorily calculated using time-dependent density functional theory. Whilst polymethine dyes behaved exceptionally, the calculated transition energies for cyanines, oxonols and various related dyes were systematically too large. Broken-symmetry unrestricted density functional calculations revealed the biradical character of several quinoid compounds derived from *p*-quinodimethane as well as that of some non-Kekulé-type structures.

1. Introduction

Current dye applications extend far beyond their use for the coloration of bulk materials. As functional dyes they are utilised as optical switches, light emitting diodes, photovoltaic devices, dye lasers and are applied in reprographics, photodynamic therapy and in many other fields of application [1,2]. These functional dyes enrich the many well-studied conventional and natural dyes. But independent of their occurrence or application all the dyes have one property in common: They display light absorption in the long-wavelength region of the electromagnetic spectrum. The field of application was broadened by compounds absorbing light beyond the visible region which are called near infrared absorbing dyes (NIR-dyes) [3,4]. NIR functional dyes have attracted increasing interest in recent years.

Numerical calculations of spectral data of dyes were first performed at the semi-empirical level of theory. Theoretical models in π-approximation found early wide application in dye chemistry [5,6]. As shown by Griffiths the Pariser-Parr-Pople (PPP) method is well suited for excited state calculations of different classes of dyes [7,8]. If calculations are done by few well-defined parameters the calculated transition energies may be competitive with those at a higher level of theory [9]. Nishimoto derived a modified equation for the calculation of two-centre repulsion integrals needed for PPP calculations [10]. This improved PPP approach allows the calculation of accurate absorption wavelengths of dyes in vinylogous and homologous series, for examples of cyanines [11]. Severe shortcomings of the PPP method, however, are the restriction to planar or nearly planar chromophores.

This limitation was removed by all-valence-electron methods [12]. Recent extensive studies on different dyes revealed that NDDO (neglect of nonbonded differential overlap) based calculations such as AM1 (Austin model 1), PM3 (parameterized model 3, PM5 etc.) including singly excited configurations (CIS) or calculations using the RPA (random phase approximation) are superior to calculations based on the semi-empirical CNDO and INDO Hamiltonian, such as CNDO (complete neglect of differential overlap)-CIS and INDO (intermediate neglect of differential overlap)-CIS methods [13-15]. A benchmark set of basic dyes used in a comparative study at the CNDO-CIS and INDO-CIS level was defined [16] to test the performance at this level and at higher levels of theory [14,17]. This test series consists of representative classical dyes of the indigo, azobenzene, anthraquinone, naphthoquinone, triphenylmethine and hydrazone structure. NDDO-based methods work well despite of the fact that the parameters were originally defined for ground state calculations. In this manner useful calculations at semi-empirical

* Corresponding author:
E-mail address: juergen.fabian@chemie.tu-dresden.de

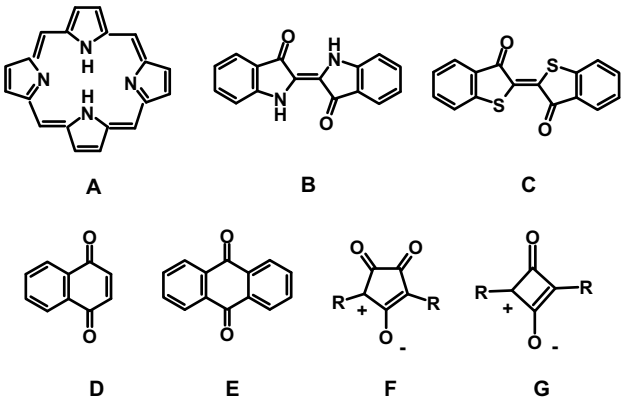
0143-7208/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.06.008

levels can be performed with very low computational expenditure. These methods are therefore generally suited in search of "tailored dyes" calculating properties of dyes over large series of compounds before more expensive higher-level methods are done.

In contrast to the above-mentioned semi-empirical methods time-dependent density functional theory (TDDFT) is a first-principles method without any empirical spectroscopic parameters [18]. It has successfully filled the gap between semi-empirical and *ab initio* methods in recent years. TDDFT methods are computationally more expensive than semi-empirical methods but allow easily studies of dye molecules of medium size. Full TDDFT calculations become more time-consuming with dyes of more than 100 atoms of second row elements. The approximate TDDFTB method, however, also allows the calculation of large chromophores [19]. TDDFT studies are not restricted to dyes in their singlet excited states. Moreover, this method allows one to study more complex photophysical processes following spectral excitation, such as deactivation processes [20]. Guillamount and Nakamura early tested the performance of TDDFT [17] with the above mentioned test series of semi-empirical calculations [16]. Except for triphenylmethine dyes experimental absorption wavelengths of low-energy electronic transitions were well reproduced.

The parent compounds of dyes in Scheme 1 stand for classes of dyes intensely investigated recently by TDDFT. Porphin (**A**) and porphyrin dyes belong to the natural dyes early studied by Sundholm [21] and Grimme [22]. Extensive studies were done on various classical dyes of industrial interest. Jaquemin et al. reported results of TDDFT calculations of conventional dyes with a series of publications. They studied indigo (**B**) [23], thioindigo (**C**) [24], naphthoquinone (**D**) [25] and anthraquinone (**E**) [26] and a large number of their derivatives. Taking solvation effects into account the calculations resulted in remarkably accurate transition energies. The numerical data within series of related compounds were additionally improved by least square fits adjusting theoretical to experimental data. The mesoionic croconaines **F** and squaraines **G** (R=aryl, heteroaryl) are functional dyes that absorb either in the visible or in the near infrared region of the spectrum. These dyes were also broadly studied by TDDFT [27]. The calculated excitation energies, however, were in less good agreement with the experimentally determined values.

Disappointing results were reported with first calculations of polymethine dyes [9,28]. Unexpectedly the TDDFT failed to reproduce the spectral data of the intense long wavelength absorption of streptopolymethine cyanines. The transition energies of these most simple polymethine dyes absorbing in the NUV, Vis or NIR region were grossly overestimated. The calculated absorption wavelengths are therefore much too low. The same problem was encountered with some heterocylic cyanines [29] and with triphenylmethine dyes [17]. Apart from cyanine-type dyes erroneous results were noticed for anionic oxonol-type polymethine dyes [9], and for colored hydrazones [14] and polyacenes [30].



Scheme 1. Natural, classic and functional dyes extensively studied by TDDFT.

The practical users of quantum chemical methods are interested to know the range of applicability of TDDFT in calculating dyes. An extensive comparison of calculated and measured observables will increase the confidence in the method. The aim of this study is to unveil strengths and limitation of TDDFT in calculating different types of colored compounds. No attempts have been made, however, to reproduce spectral data as accurately as possible but rather to detect stronger deviations between theory and experiment. In addition to some conventional dyes the study includes colored compounds of non-Kekulé, mesoionic and biradicaloid character and compounds twisted about double bonds. In contrast to former studies recently carried out on classical dyes the series of dyes is heterogeneous.

2. Computational

To calculate ground state geometries and excitation energies the Kohn–Sham density functional theory (DFT) and time-dependent DFT (TDDFT) were employed, respectively [18]. Calculating the frequency dependence of a time-dependent electrical field perturbation excitation energies and transition probabilities are obtained without calculating the excited states themselves. The performance of TDDFT depends on the approximate exchange and correlation functional (xc-functional) and the basis set.

Numerous functionals have been proposed for DFT calculations. The well-known and broadly used Becke3–Lee–Yang–Parr hybrid functional (B3LYP) was favored in this study over the parameter-free Perdew–Burke–Enzerhof hybrid functional (abbreviated as PB0 or PBE1PBE). The PB0-functional was recommended by Jaquemin et al. in studies of classical dyes. In critical cases, however, both functionals were used in this study.

The most frequently employed Pople-type Gaussian-type basis sets in DFT calculation is the valence double-ξ basis set 6-31 + G*. Smaller basis sets are generally less suited. To achieve convergence in the calculated $\pi \rightarrow \pi^*$ transition energies more extended basis sets were used by Jacquemin et al. The standard basis set 6-31 + G* was generally employed in the calculation of the optimum geometry and the spectral excitation and more extended basis sets only if the results were unsatisfactory. Since the aim of this study was not to accurately reproduce numerical values but rather to screen a large number of different chromophoric compounds the simplified theoretical model appears adequate. Solvent effects were disregarded although the calculation may improve the transition energy of dyes calculated at too short wavelengths. However, the solvents used in the spectroscopic studies of the selected dyes vary greatly. As far as possible, spectral data were selected in less polar solvents. According to former studies the mean absolute error (MAE) of the calculated TDDFT excitation energies without consideration of the solvent effect amounts to about 0.21 eV [9,17].

DFT calculations were generally carried out with the spin-restricted RDFT approach for closed shell and with the spin-unrestricted UDFT approach for open shell compounds. Mixing of the HOMO and the LUMO in the initial approximation may destroy the α/ß-spatial symmetry resulting in spin-broken symmetry (BS) solutions. The expectation value $<S^2>$ of the S^2 spin operator calculated by BS-UDFT serves as a diagnostic parameter [31]. This value is generally zero or very low, e.g. for long chain polymethines. If appreciably larger than 0 the biradicaloid character of the dye is indicated. For $<S^2>$ values of about 1 the singlet and triplet states are close in energy. In this case typical spectra of triplet species are recorded [32]. Michl introduced the term biradicaloid for compounds with approximately degenerate non-bonding

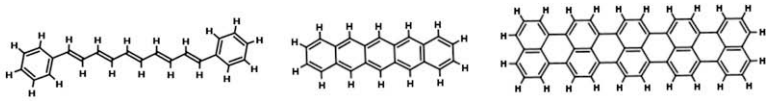
molecular orbitals that are occupied by two electrons [33]. Due to the low HOMO–LUMO gap NIR dyes are potentially biradicaloid. In this case doubly excited configurations in addition to the singly excited configurations are at least required for the proper description of the biradical species. However, TD-DFT is essentially a single-configurational approach. Therefore a strong biradical character of dyes may result in poor excitation energies.

The routinely calculated electronic transitions are vertical transitions. They approximately correspond to experimental band maxima in low-resolution electronic spectra. Since the absorption range over a large wavelength region in going from the visible to the near infrared, the spectral data and errors are preferably given in eV. In critical cases the bulk solvation effect was considered by the well-known polarizable continuum model (PCM).

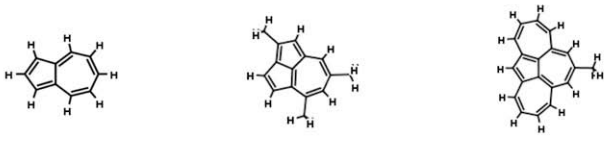
For comparison spectral data were also calculated by the semi-empirical PPP (Pariser–Parr–Pople) and by Zerneŕs spectroscopy oriented INDO-CIS (ZINDO/S, Intermediate Neglect of Differential Overlap) [12] taking into accounts up to 225 configurations and all singly excited configurations, respectively. The geometry of the semi-empirical calculations is the same as in TDDFT calculations. PPP calculations were only performed for compounds with strictly planar conjugated systems. TDDFT and INDO-CIS calculations were carried out by the GAUSSIAN03 suit of programs [34] and PPP calculations by the WFPPP program, Version 2009,01 [35]. CIS and SAC-CI (symmetry adapted cluster) calculations [36] were preformed by GAUSSIAN03 [34] and TDDFT/TDA (Tamm–Dancoff approximation) and SORCI (spectroscopy oriented configuration interaction) calculations [37] by the ORCA program package [38].

3. Results

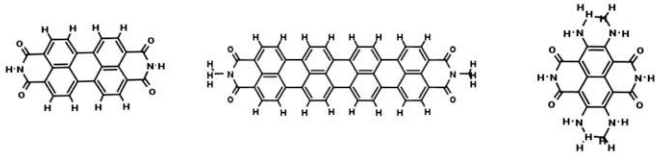
To extend knowledge concerning the scope and limation of TDDFT 130 chromophoric compounds were randomly selected and calculated. The performance of TDDFT in calculating transition energies varies considerably. Classical and functional dyes are discussed first. Less common colored compounds of multiple charge and higher multiplicity are finally considered. The results of the calculations were collected in the Figs. 1–3. The lowest-energy transitions are only listed. The are intense in most cases.



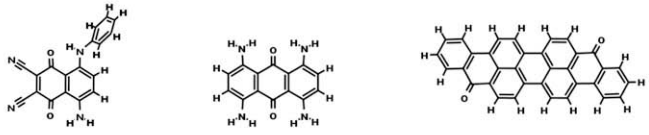
	1		**2**		**3**	
TDDFT	453 (2.93)	*2.74*	648 (0.04)	*1.91*	803 (1.70)	*1.54*
Exp	403 (4.97[6]	*3.08*	585 (2.12) [89]	*2.12*	747 nm [90]	*1.66*
Deviations		*-0.34*		*-0.21*		*-0.21*
INDO-CIS	2.83 (2.82)		2.36 (0.27)		1.86 (2.36)	
PPP-CIS	2.47 (3.22)		2.42 (0.33)		1.74 (3.10)	



	4		**5**		**6**	
TDDFT	522 (<0.01)	*2.38*	689 (<0.01)	*1.80*	1356(<0.01)	*0.91*
Exp	581 (2.51)[89]	*2.13*	650 (1.89)[89]	*1.91*	1630 1.40 [91]	*0.76*
Deviations		*+0.25*		*-0.11*		*+0.15*
INDO-CIS	2.11 (0.02)		1.85 (<0.01)		1.19 (<0.01)	
PPP-CIS	1.88 (0.02)		1.44 (<0.01)		0.87 (0.01)	



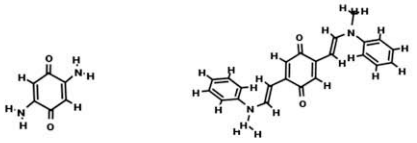
	7		**8**		**9**	
TDDFT	522 (0.64)	*2.38*	767 (1.63)	*1.62*	565 (0.29)	*2.19*
Exp	526 (4.91)[92]	*2.36*	762 (5.21)[93]	*1.63*	629 (4.56)[43]	*1.97*
Deviations		*+0.02*		*-0.01*		*+0.22*
INDO-CIS	2.62 (1.15)		1.91 (2.26)		2.50 (0.49)	
PPP-CIS	2.54 (1.51)		1.80 (2.87)		2.41 (0.62)	



	10		**11**		**12**	
TDDFT	687 (0.21)	*1.81*	583 (0.32)	*2.13*	571 (0.89)	*2.17*

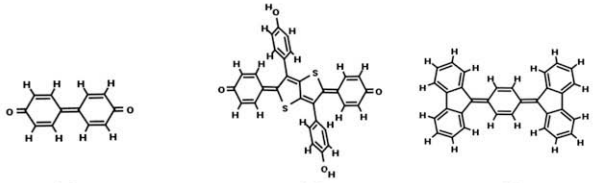
Fig. 1. Spectral data of natural, conventional and functional dyes: calculated and experimental absorption wavelengths in nanometers (theoretical oscillator strengths *f* and experimental *lg*ε values in parentheses) and calculated excitation energies and deviations between theory and experiment in eV (TDDFT)[a]. For comparison transition energies and *f*-values (in parentheses) of semi-empirical calculations are added [4,6,9,43,47,89–106].

Exp	760 (3.69)[4] *1.63*	620[94] *2.00*	588 (4.62)[6] *2.11*
Deviations	*+0.18*	*+0.13*	*+0.06*
INDO-CIS	2.18 (0.29)	2.50 (0.58)	2.38 (1.47)
PPP-CIS		2.44 (0.56)	2.31 (1.88)



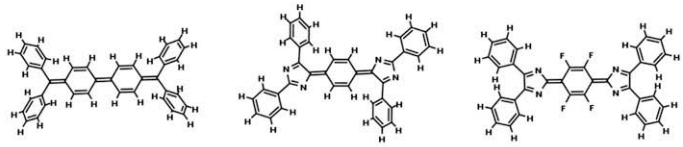
13 **14** **15**

TDDFT	474 (0.00) *2.62*	660 (0.00) *1.88*	542 (0.03) *2.29*
Exp	488 (2.42)[89] *2.54*	725 (3.67)[4] *1.71*	581 (4.26)[89] *2.13*
Deviations	*+0.08*	*+0.17*	*+0.16*
INDO-CIS	2.61 (0.00)	2.25 (0.0)	2.47 (0.11)
PPP-CIS	2.35 (0.00)		2.04 (0.04)



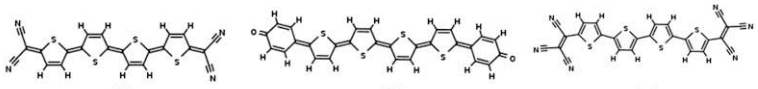
16 **17** **18**

TDDFT	392 (1.06) *3.16*	618 (0.62) *2.01*	537 (1.51) *2.29*
Exp	386 (4.5)[6] *3.21*	634 (4.71)[95] *1.96*	573 nm [96] *2.16*
Deviations	*-0.05*	*+0.05*	*+0.13*
INDO-CIS	2.95 (1.86)	1.93 (2.66)	2.25 (1.97)



19 **20** **21**

TDDFT	654 (2.10) *1.89*	739 (1.19) *1.68*	678 (2.16) *1.83*
Exp	574 (5.02) [97] *2.16*	~670 (~4.8)[98] *1.85*	609 (5.04) [47] *2.04*
Deviations	*-0.27*	*-0.17*	*-0.21*
INDO-CIS	1.73 (2.79)	1.72 (2.00)	1.70 (2.91)



22 **23** **24**

TDDFT	765 (2.30) *1.62*	904 (2.81) *1.37*	644 (1.90) *1.92*
Exp	790[99] *1.57*	830 (4.45) [100] *1.49*	610 nm [101] *2.03*
Deviations	*+0.05*	*-0.12*	*-0.11*
INDO-CIS	1.95 (2.89)	1.61 (3.66)	1.91 (2.05)
PPP-CIS	1.98 (2.38)	1.23 (9.00)	2.36 (2.50)

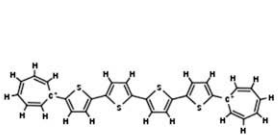
Fig. 1. (*continued*).

3.1. Conventional chromophoric compounds

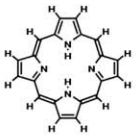
The dyes **1–42** involve representatives of polyene, acene, rylene, perylene, quinone, porpyrin, indigo and azo dyes (Fig. 1). These dyes are either mostly natural dyes occurring in plants, classic synthetic dyes used for coloration or functional dyes studied for innovative applications. The mean absolute error (MAE) of the calculated TDDFT transition energies with respect to the experimental energies amounts to 0.14 eV. An error of this order of magnitude was expected in view of the simplified theoretical model and the neglect of the solvent effect [23–26].

Whereas the calculated excitation energies are frequently larger than the experimental ones ω,ω′-diphenylpentaene (**1**) behaves different. In this case the calculated excitation energy is too low by 0.34 eV. Since the B3LYP functional overestimates the electron delocalization [39], the real bond length alternation (BLA) has to be considered. This was approximately done by TDDFT calculations using the BH and HLYP functional with a stronger amount of Hartree–Fock exchange and by *ab initio* HF calculations. The error is reduced to 0.19 eV and 0.03 eV, respectively. The same problem encountered with other polyenic structures [40]. However, in general the B3LYP functional is useful.

The first transition of the red pentacene (**2**) is well reproduced in this study. Satisfactory TDDFT results were obtained for oligoacenes [41] but a more close examination of the lowest-energy transitions revealed shortcomings [30]. Acenes and rylenes display absorptions up to the NIR [5]. Rylene (**3**) was accurately calculated. Non-alternant hydrocarbons, such as **4–6**, exhibit long wavelength absorptions. Examining the blue azulene (**4**) Michl and Thulstrup revealed the origin of its deep color [42]. The extremely low

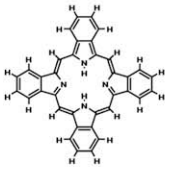


25

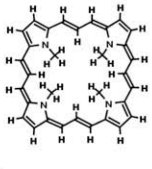


26

			Q (av.)			*B (av.)*	
TDDFT	715 (2.23)	*1.73*	546 (<0.01)	*2.27*	374 (0.49)	*3.31*	
Exp	652 (4.17) [102]	*1.90*	526 (~4.0)	*2.36*	397(5.42)[6]	*3.12*	
Deviations		*-0.17*		*-0.09*		*+0.19*	
INDO CIS	1.67 (2.41)		1.77 (0.04)		3.25 (2.02)		
PPP-CIS	1.82 (2.76)		1.83 (0.04)		3.54 (2.38)		

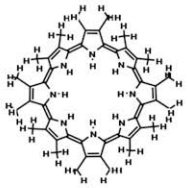


27

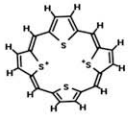


28

	Q (av.)		*B (av.)*		*A (deg)*		*B (deg)*	
TDDFT	597 (0.11)	*2.08*	401 (1.11)	*3.09*	852 (<0.01)	*1.46*	487 (1.86)	*2.55*
Exp	605 nm (~3.9)	*2.05*	430 (5.34) [6]	*2.88*	783 (4.45)	*1.28*	547 (5.96)[103]	*2.27*
Deviations		*+0.03*		*+0.21*		*+0.18*		*+0.28*
INDO CIS	1.56 (0.32)		3.18 (2.37)		1.13 (<0.01)		2.50 (3.79)	
PPP-CIS	1.74 (0.13)		3.04 (3.79)					

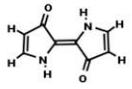


29

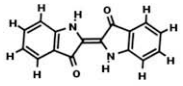


30^{++}

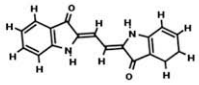
	A (deg.)		*B (deg.)*			
TDDFT	913 (0.55)	*1.36*	412 (1.12)	*3.01*	587 (<0.01)	*2.11*
Exp	1112 (5.12) [104]	*1.11*	431 (4.90)	*2.88*	646 (3.63) [9]	*1.92*
Deviations		*+0.25*		*+0.13*		*+0.19*
INDO CIS	0.95 (0.72)		2.80 (3.58)		1.52 (<0.01)	



31



32



33

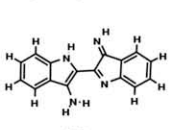
TDDFT	473(0.17)	*2.62*	553 (0.28)	*2.24*	531 (0.60)	*2.33*
Exp	529 (3.83)[6]	*2.34*	605 (4.30)[6]	*2.05*	573(4.35)[6]	*2.16*
Deviations		*+0.28*		*+0.19*		*+0.17*

Fig. 1. (*continued*).

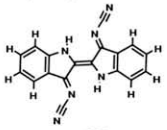
transition energy of **6** corresponds to a weak absorption recorded in the NIR (1630 nm). TDDFT was also well suited to calculate rylene derivatives, such as 1,8-naphthalimide dyes, which are particularly stable functional dyes, e.g. **7** and **8**. The deeply colored **9** may be considered as a derivative of naphthalimide [43]. A series of 39 dyes of this structure have been recently investigated by TDDFT [44].

The compounds **10**–**15** are amino-substituted anthraquinone, naphthoquinone and benzoquinone dyes. The naphthoquinone **10** was one of the early prepared NIR absorbing quinone dyes. The lowest-energy transition of 2,5-diaminoquinone (**13**) is dipole forbidden. This is no longer the case for the related more extended compound **14**. Jacquemin et al. investigated a large number of substituted naphthoquinone [25] and anthraquinone dyes [26]. Anthraquinone dihydroxy derivatives were recenly studied in detail [45]. The spectral data of these compounds were well reproduced with extended basis sets and consideration of the solvent effects. The colored compounds **16**–**21** are also of quinoid structure. Compound **17** is sterically crowded. The structures **18, 20** and **21** may be considered as derivatives of *para*-quinodimethane. The synthetic compound contains eight tert-butyl groups. These groups were replaced by hydrogens in the calculation. The calculated transition energies agree well with the experimental values. The violet compound **19** is called Chichibabin's hydrocarbon. The detection of paramagnetic species suggested a biradicaloid compound [46]. The unusual experimental behavior of this hydrocarbon was attributed to the presence of a thermally accessible higher energy paramagnetic state, separated by 2–3 kcal/mol from the diamagnetic singlet ground state. According to BS-UDFT

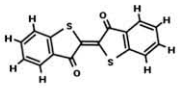
INDO-CIS	3.03 (0.38)	2.87 (0.47)	2.93 (1.03)
PPP-CIS	2.52 (0.51)	2.45 (0.71)	2.40 (1.32)



34

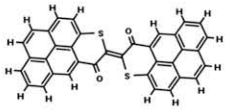


35

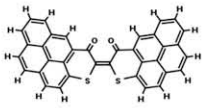


36

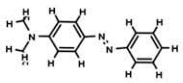
TDDFT	621 (0.22) *2.00*	645 (0.34) *1.92*	530 (0.21) *2.34*
Exp	617 (3.95)[6] *2.01*	751[105] *1.65*	546(4.26)[6]) *2.29*
Deviations	*-0.01*	*+0.27*	*+0.05*
INDO-CIS	2.39 (0.44)	2.46 (0.58)	3.76 (0.39)
PPP-CIS	1.91 (0.36)	1.99 (0.75)	2.33 (0.47)



37

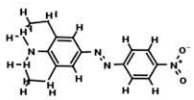


38

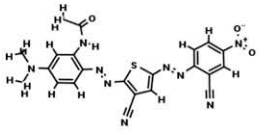


39

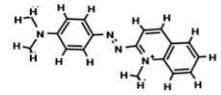
TDDFT	702 (0.78) *1.77*	625 (0.49) *1.98*	398 (0.91) *3.12*
Exp	728 (4.52) [106] *1.70*	584 (4.22)[106] *2.12*	400 (4.49)[6] *3.10*
Deviations	*+0.07*	*+0.14*	*+0.02*
INDO-CIS	2.62 (1.13)	3.11 (0.77)	3.11 (1.03)
PPP-CIS	1.91 (1.20)		3.09 (1.27)



40



41



42^{+}

TDDFT	491(0.86) *2.53*	659 (1.51) *1.88*	524 (0.17) *2.37*
Exp	518 4.53 [6] *2.39*	706 nm [4] *1.76*	591 5.00[6] *1.69*
Deviations	*+0.14*	*+0.12*	*+0.68*
INDO-CIS	2.77 (1.18)	1.74 (1.70)	2.31 (1.07)
PPP-CIS	2.89 (1.35)	2.22 (1.84)	

[a] TDDFT/6-31+G*//DFT/6-31+G* calculations, except for **1**, **12**, **37**, **47**, **48**, **49**, **63**, **64**, **76**, **81**, **113** and **114**. Because of convergence problems, diffuse functions were omitted in these cases. TDDFT/3-21+G* calculations were performed for the relatively large compounds **3**, **19**, **21** and **48**. In the case of **17**, **22**, **23**, **24**, **28, 29** and **101** extended aliphatic groups were replaced by methyl groups or by hydrogen. Forbidden or very weak low-energy transitions without experimental support were disregarded. The formulas were drawn according to the calculated geometries by means of the MARVIN graphics program: MarvinSketch 5.1.1, ChemAxon Ltd, 2008. Since molecular charges are partly hidden in this presentation, charges are additionally marked with numbers of the formulas. Two charges indicate zwitterionic and dots radicalic structures.

Fig. 1. (*continued*).

calculations the compounds is singlet/triplet unstable with an expectation values $<S^2>$ of 0.50 (single point calculation using the basis set 6-31 + G*). Without consideration of doubly excited configurations the transition energy is overestimated by 0.27 eV. The compounds **20** and **21** [47] are also biradicaloid ($<S^2>$-values of 0.35 and 0.30, respectively). In good agreement with the experiment these compounds absorb at longer wavelengths than **19**. The greenish-blue **21** is known to exist mainly in the singlet ground state and is paramagnetic in solution to 0.1% [47,48].

The lowest-energy transitions of the four deeply colored acceptor-substituted quaterthiophenes **22–25** are very well reproduced (cf. Fig. 1). The wavefunctions of the quinoid oligomers **22** and **25** are again biradicaloid. Single point BS-UDFT calculations of **22** and **23** provided $<S^2>$-values of 0.39 and 0.26, respectively. The formulas of these compounds of Fig. 1 do not visualize the biradicalic nature of the compounds. Interestingly, the solution of a substituted **22** is discolored to a faint gray [49]. No noticeable absorptions were actually found in the visible region. In good agreement with this result the TDDFT calculation **22** exhibits only very weak transitions in the visible region ($f < 0.05$). Higher homologs of **22** display equilibria between the quinoid singlet ground state molecules and ESR active species. A theoretical study of long chain quinoid oligothiopenes end-capped with dicyanoethylene reveiled a rapid increase of the biradicaloid character and energetic stabilization of the spin-contaminated open-shell structure relative to the closed shell singlet structure [50].

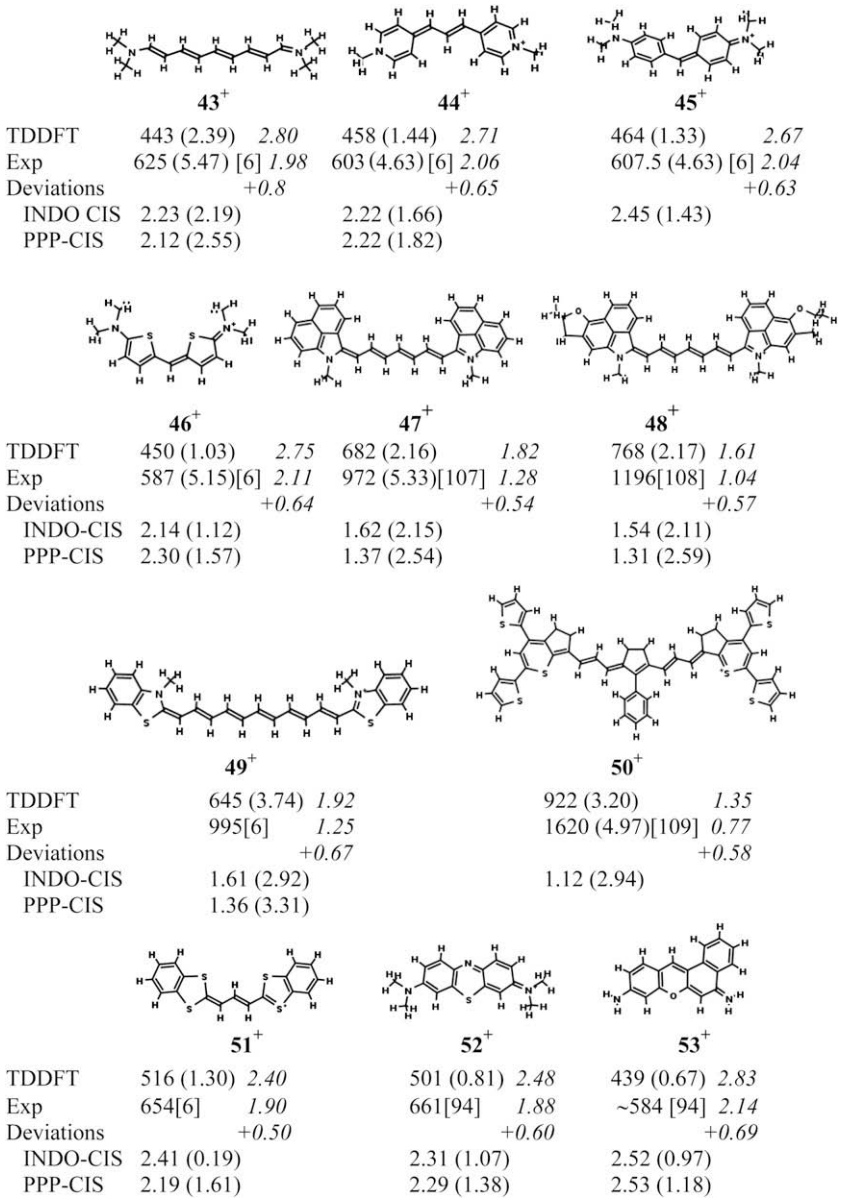


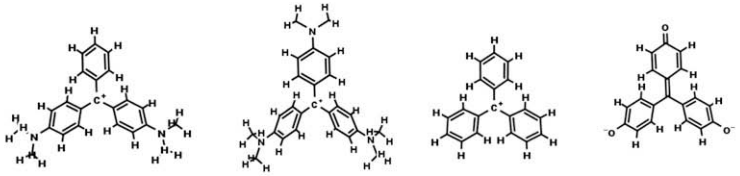
Fig. 2. Spectral data of polymethine dyes. See heading and footnotes of Fig. 1 [4,6,55,58,94,97,105,107–118].

Porphin and porphyrinoids are exemplified with **26–30**. The deeply red free-base porphin is the most simple representative of this series. The weak low-energy Q_x and Q_y transitions of porphin (averaged excitation energies denoted as Q in Fig. 1) and the intense B_x and B_y (averaged as far as resolved, denoted as B) are reasonably well calculated by TDDFT. A good agreement was also found in previous studies [21,22]. In contrast to porphin and related compounds and in disagreement with the theory the long-wavelength absorption of the puckered cylo[8]pyrrol **29** is intense (cf. Fig. 1). Such cases are rare und not yet understood. The dication of the tetrathiaporphyrin **30** is a bowle-shaped molecule giving rise to a deep green color in solution.

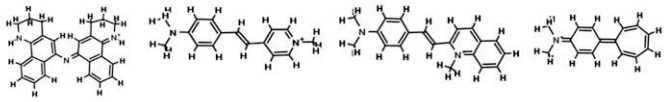
Spectral data of indigo and thioindigo dyes are well reproduced by TDDFT [23,24]. The dyes **31** and **33–38** are closely related to indigo (**32**) and **37** and **38** to thioindigo (**36**). The deviations of the calculated from the experimental values are small. The color band of the vinylogous indigo **33** is correctly calculated to be blue-shifted relative to indigo **31**. In contrast, substitution of the carbonyl groups of indigo by cyanoimino groups to **35** brings about a marked red-shift. The experimental transition energies of isomeric pyrenoindigo dyes **37** and **38** are also well reproduced. In contrast to the *cis*-isomer the *trans*-isomer absorbs in the infrared. The dyes **39**-**40** are mono azo dyes absorbing in the visible region whereas the bisazo dye **41** absorbs in the NIR [51]. Theory and experiment differ by only 0.07 eV on average. Satisfactory results were also reported for a large number of azo dyes [52]. Although the deviations of the compounds **28, 29, 31 and 35**, are nearly 0.3 ev, the mean absolute deviation of the compounds **1–41** amounts to only 0.15 eV. A poor result was, however, obtained for the cationic azo dye **42**$^+$. But this compound is not an intrinsic azo dye but rather a diaza-substituted cyanine dye. Cyanine dyes are considered in the following section.

3.2. Problematic cases: polymethine dyes

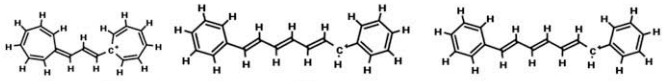
In sharp contrast to the above reported results spectral data of polymethine dyes are very poorly predicted by TDDFT. These dyes exhibit a strong systematic error. TDDFT calculations of the cationic



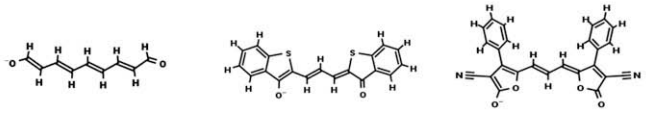
	54^{+}		**55**$^{+}$		**56**$^{+}$		**57**$^{-}$	
TDDFT	490 (0.86)	*2.53*	486 (0.69)	*2.55*	381 (0.35)	*3.26*	458 (0.56)	*2.71*
Exp	621 (5.02)[6]	*2.03*	585[6]	*2.12*	431[6]	*2.88*	531[6]	*2.12*
Deviations		*+0.50*		*+0.43*		*+038*		*+0.59*
INDO-CIS	2.57 (0.99)		2.68 (0.84)		3.23 (0.51)		2.55 (0.83)	



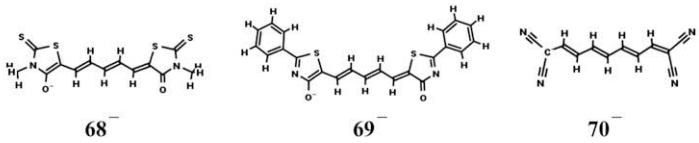
	58^{+}		**59**$^{+}$		**60**$^{+}$		**61**$^{+}$	
TDDFT	675 (0.59)	*1.84*	476 (1.26)	*2.61*	497 (1.16)	*2.50*	476 (0.76)	*2.61*
Exp	830 (4.98) [110]	*1.49*	476[55]	*2.61*	528 [94]	*2.35*	569 4.56[111]	*2.18*
Deviations		*+0.35*		*+0.00*		*+0.15*		*+0.64*
INDO CIS	1.53 (0.98)		2.46 (1.42)		2.40 (1.43)		2.62 (0.43)	



	62^{+-}		**63**$^{+}$		**64**$^{-}$	
TDDFT	502(1.33)	*2.47*	496 (2.32)	*2.50*	497 (2.25)	*2.49*
Exp	713 (4.88)[107]	*1.73*	622[112]	*1.99*	610 (5.11)[112]	*2.07*
Deviations		*+0.74*		*+0.51*		*+0.42*
INDO CIS	2.03 (1.64)		2.19 (2.32)		2.02 (2.05)	
PPP-CIS	2.01 (1.82)		1.97 (2.43)		1.98 (2.43)	



	65^{-}		**66**$^{-}$		**67**$^{-}$	
TDDFT	404 (1.90)	*3.07*	531 (1.13)	*2.34*	573 (1.40)	*2.16*
Exp	548 (4.80)[6]	*2.26*	650[6]	*1.90*	716 (5.08)[107]	*1.73*
Deviations		*+0.81*		*+0.44*		*+0.43*
INDO CIS	2.37 (1.96)		2.32 (1.46)		1.77 (1.64)	
PPP-CIS	2.30 (2.33)		2.12 (1.72)			



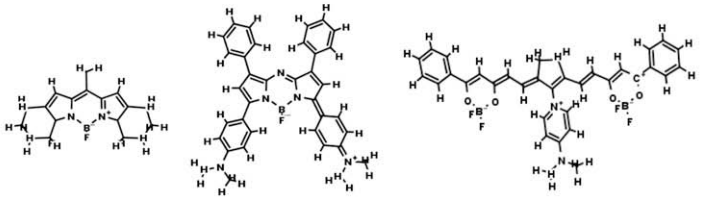
68^{-} **69**$^{-}$ **70**$^{-}$

Fig. 2. (*continued*).

cyanine dyes **43**$^{+}$**–56**$^{+}$ provide considerably too low excitation energies (Fig. 2). The bad performance of the method was first realized with the most simple cationic chain compounds known as streptopolymethine cyanines [9,28]. TDDFT calculations of parent cyanines studied experimentally up to the tridecamethine were performed by different theoretical models varying both the functionals and basis sets (Table 1). The effect of the theoretical model was very small. The calculated absorption wavelengths are severely underestimated in all cases. The calculated TDDFT transition energies are about 0.5–0.8 eV too large. For example, the nonamethine streptocyanine **43**$^{+}$ was predicted at 2.80 eV (443 nm) whereas the experimental excitation energy amounts to 1.95 eV (635 nm). The error in wavelengths increases from 7 nm for monomethine to 294 nm for tridecamethine (cf. Table 1). Absorptions of parent polymethine cyanines in the visible region are predicted in the ultraviolet and those in the near infrared are predicted in the visible region. The experimentally found "vinylene shift" of about 100 nm is not reproduced.

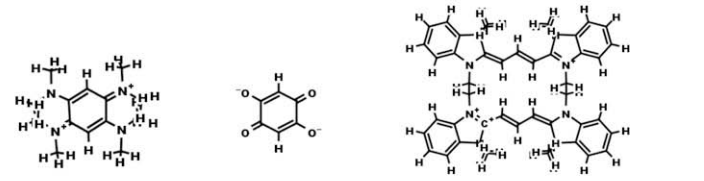
The simplified so-called Tamm–Dancoff approximation to TDDFT and the approximate TDDFTB method [53] obviously inherit the disadvantages of the full TDDFT. According to Table 1 the results of the TDDFTB calculations are just as bad as the result obtained by full TDDFT. Studies by double-hybrid density functional theory using the B2LYP functional also failed [54]. It should be mentioned that PCM-TDDFT calculations of the solvent effect did not remove the discrepancy. Undecamethine cyanine, for example, undergoes a solvent-induced red shift from 501 nm (gas phase) to 544 nm (in CH_2Cl_2). The shift is not sufficient to reproduce the experimental

TDDFT	532 (1.87) *2.33*	687 (1.23) *1.80*	473 (2.18) *2.62*
Exp	714[6] *1.73*	781[6] *1.58*	632 [6] *1.96*
Deviations	*+0.60*	*+0.22*	*+0.66*
INDO-CIS	2.15 (1.79)	1.88 (1.37)	2.04 (2.07)
PPP-CIS	1.88 (2.27)	1.63 (1.93)	1.98 (2.38)



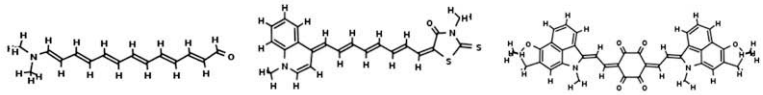
71 **72** **73**

TDDFT	443 (0.54) *2.80*	688 (0.75) *1.80*	589 (2.60) *2.10*
Exp	535 [58] *2.32*	799 (4.94)[113] *1.55*	893 (5.28)[114] *1.39*
Deviations	*+0.48*	*+0.25*	*0.71*



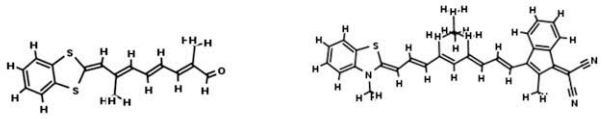
74^{++} **75^{--}** **76^{++}**

TDDFT	553 (0.02) *2.24*	466 (0.00) *2.66*	602 (<0.01) *2.06*
Exp	573[97] *2.16*	496[6] *2.50*	590 (3.98)[115] *2.20*
Deviations	*+0.08*	*+0.16*	*-0.14*
INDO CIS	1.90 (0.05)	2.60 (0.00)	2.32 (0.03)
PPP-CIS		2 40 (0.00)	2.10 (0.04)



77 **78** **79**

TDDFT	491 (2.31) *2.53*	564 (2.17) *2.20*	697(1.58) *1.78*
Exp	513 (4.86)[6] *2.42*	607[4] *2.12*	813 (5.25)[108] *1.52*
Deviations	*+0.03*	*+0.08*	*+0.26*
INDO CIS	2.65 (2.66)	2.29 (2.12)	2.25 (1.93)
PPP-CIS	2.14 (2.92)	1.94 (2.62)	



80 **81**

TDDFT	439 (1.72)	*2.82*	739 (1.59) *1.68*

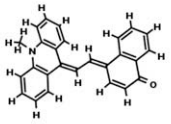
Fig. 2. (*continued*).

absorption wavelength of 735 nm. Plotting calculated versus experimental absorption wavelengths revealed, however, that the strong deviations from the experiment are systematic. Surprisingly good absorption wavelengths resulted from the last square fit (cf. Table 1).

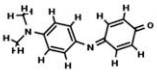
The shortcomings in calculations of the parent cyanines are not observed at the *ab initio* level of theory. Apart from the well-known failure at the RHF level higher level *ab initio* calculations such as SCS (spin-component scaled)-CI(D) or CASPT2 (complete active space with second-order perturbation theory) predicted considerably longer wavelengths of the color band than TDDFT and vinylene shifts more close to the experimental 100 nm shift. Estimates by the multiconfigurational methods SAC (symmetry-adapted-cluster)-CI and SORCI (spectroscopy oriented CI) were promising with useful results already obtained by small basis sets (cf. Table 1).

The discrepancy found with the most simple chain compounds is similarly encountered with more complex cyanine dyes. The bispyrido trimethine (**44^+**) and diaminophenyl monomethine (**45^+**) contain the nonamethine chain of **43^+** as substructure. The dyes therefore absorb at similar wavelengths. Almost equal wavelengths were also calculated for both compounds but again the transition energies are about 0.65 eV in error. Thus the deviation is again systematic. As shown with **46^+**–**51^+** TDDFT fails more generally in calculating polymethine dyes with heterocyclic end groups. The dye **50^+** is one of the most bathochromic cyanine dyes. The calculated wavelength, however, amounts to only 920 nm in the λ-scale, corresponding to an error of 0.58 eV.

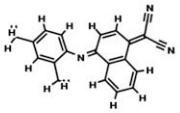
Exp	456 (4.64) [116]	*2.72*		810 (4.64) [109]	*1.53*	
Deviations		*+0.01*			*+0.15*	
INDO-CIS	3.05 (2.08)			1.97 (1.34)		
PPP-CIS	2.38 (2.26)					



82

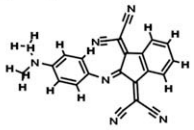


83

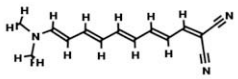


84

TDDFT	506 (0.89)	*2.45*		542 (0.44)	*2.29*		668 (0.54)	*1.85*
Exp	525 (4.4)[107]	*2.37*		545 (4.08) [117]	*2.27*		761 (4.41)[4]	*1.63*
Deviations		*+0.08*			*+0.02*			*+0.22*
INDO-CIS	2.55 (1.41)			2.42 (0.45)			2.15 (0.66)	



85



86

TDDFT	663 (0.20)	*1.87*		470 (2.20)	*2.64*	
Exp	755 (4.41)[105]	*1.64*		~500[118]	*2.48*	
Deviations		*+0.23*			*+0.16*	
INDO-CIS	1.98 (0.29)			2.55 (2.22)		
PPP-CIS				2.33 (2.54)		

Fig. 2. (*continued*).

An overestimation of the transition energy is not only found for symmetric dyes but also for less symmetric ones, such as **52**$^+$ and **53**$^+$. Furthermore, the transition energies were overestimated for cationic triphenylmethine dyes **54**$^+$**–56**$^+$. This finding is in agreement with previous studies [14,17]. The compounds **58**$^+$–**61**$^+$ are related to cyanine dyes. The hemicyanines **59**$^+$ and **60**$^+$ were the only dyes of the cyanine series calculated with a reasonably good accuracy. The results of calculations of hemicyanines with the pyridine nucleus, such as **59**$^+$, were performed with consideration of the solvent effect by PCM and application of the linear regression approach [55]. The result of the calculation of the carbopolymethine **62**$^+$ is again unsatisfactory.

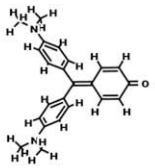
Apart from previous TDDFT calculations of parent cyanines [9,28] few studies dealt only with cyanine dyes so far [29,56]. Deviations between 0.38 and 0.53 eV were reported in the literature for heterocyclic cyanines [29]. In view of poor results on indocyanine dyes the B3LYP functional was replaced by BLYP [56]. A thiacarbocyanine has also been calculated by the BHandHLYP functional [57]. However, as shown in Table 1 for the streptopolymethine cyanines neither BLYP nor BHandHLYP can overcome the dilemma.

Interesting cases are the related carbomethines **63**$^+$ and **64**$^-$. These dyes contain the same conjugated system but differ in their molecular charge. Inspite of the different charge the experimental as well as the calculated transition energies are nearly the same. However, the calculated and experimental values differ again by 0.5 eV. Thus the error of the calculation of the cyanine dyes is obviously not due to the molecular charge. TDDFT also fails for negatively charged polymethine dyes (oxonol dyes). Compound **65**$^-$ is a representative of the vinylogous parent oxonol dyes whereas **66**$^-$–**69**$^-$ are more complex heterocyclic oxonols. The deviations of **65**$^-$**–69**$^-$ are again large and amount to 0.5 eV on average. A similar error was found for the related anionic dye **57**$^-$. Replacement of the carbonyl groups of **65**$^-$ by dinitrilomethylene groups results in **70**$^-$. The error of this compound amounts to 0.69 eV and is therefore nearly as large as for the related oxonol parent dye **65**$^-$ (0.81 eV).

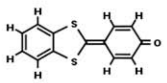
The transition energy of **71** which exemplifies a neutral azadipyrromethene boron complex [58] is overestimated by 0.5 eV. A similar deviation was reported for a related laser dye [59]. Consideration of the solvent effect did not remove the discrepancy. The error was considerably less for the aryl-subsituted azadipyrromethene boron complex **72**. A strong bathochromic effect of 0.38 eV by dimethylamino groups was predicted relative to the unsubstituted tetraphenyl azadipyrromethene boron complex. This result is supported by the experiment (0.36 eV). A close agreement beween theory and experiment was reported for dyes of this structure tested as photodynamic therapy agents [60]. The TDDFT calculation of the borine-type oxonol dye **73**$^-$ again failed. The calculated transition energy is strongly overestimated by 0.7 eV. Considering the whole series of polymethine dyes (**42**$^+$**–73**$^-$) the mean absolute deviation amounts to 0.51 eV (32 data). Thus, TDDFT in the routinely used approximations is not suited to predict absorption wavelengths of cyanine dyes.

The doubly charged compounds **74**$^{++}$ and **73**$^{--}$ may be considered as coupled cyanines and oxonols, respectively rather than as substituted quinones. The longest-wavelength absorptions of these compounds are well reproduced by TDDFT calculations. Apparantly this also holds for the bichromophoric dye **76**$^{++}$. In this case two heterocyclic pentamethines are weakly coupled giving rise to a weak longwave and an intense short wavelength band (exitonic splitting). A closer inspection revealed, however, that the good agreement between theory and experiment is fortunate. The calculated excitonic-type splitting is three times larger than the experimental one compensating the above-mentioned error in calculating cyanines.

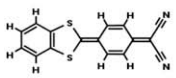
Merocyanine-type dyes take an intermediate position in structure between polymethines and polyenes. The error in the series **77–82** is considerably lower than for cyanines or vanishes entirely. The failure of the calculated transition energy of the



87

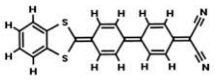


88

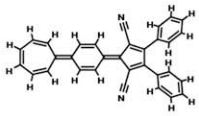


89

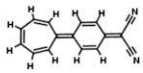
TDDFT	434 (0.61) *2.86*	384 (0.79) *3.23*	462 (1.26) *2.69*
Exp	~465[6] *2.67*	450 (4.62)[6] *2.76*	641 (4.97)[119] *1.93*
Deviations	*+0.19*	*+0.47*	*+0.76*
INDO CIS	2.76 (0.13)	2.65 (2.66)	2.73 (1.62)
PPP-CIS		2.14 (2.92)	2.39 (2.02)



90

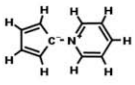


91

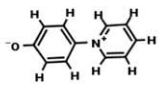


92

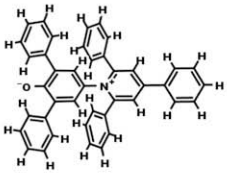
TD-DFT	613 (1.93) *2.02*	654 (1.41) *1.90*	505 (1.18) *2.45*
Exp	1045 (3.91) [119] *1.19*	934[97] *1.33*	590[120] *2.10*
Deviations	*+0.83*	*+0.57*	*+0.35*
INDO CIS	1.93 (2.66)	1.69 (1.88)	
PPP-CIS	1.72 (3.34)		2.12 (1.75)



$\mathbf{93}^{+/-}$

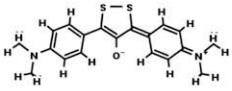


$\mathbf{94}^{+/-}$

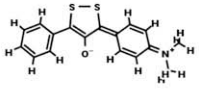


$\mathbf{95}^{+/-}$

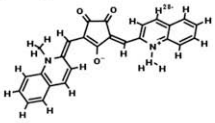
TDDFT	443 (0.38) *2.80*	489 (0.52) *2.49*	853 (0.34) *1.48*
Experiment	511 (4.34)[6] *2.43*	550[64] *2.25*	795 (~4.1)[97] *1.56*
Deviations	*+0.37*	*+0.24*	*-0.08*
INDO CIS	2.12 (0.64)	1.82 (0.65)	1.13 (0.20)



$\mathbf{96}^{+/-}$



$\mathbf{97}^{+/-}$



$\mathbf{98}^{+/-}$

TDDFT	629 (0.76) *1.97*	614 (0.53) *2.02*	710 (1.35) *1.75*
Exp	648[121] *1.91*	617[122] *2.01*	840[123] *1.48*
Deviations	*+0.06*	*+0.01*	*+0.27*
INDO-CIS	1.69 (0.90)	1.69 (0.70)	1.32 (1.50)

Fig. 3. Spectral data of assorted chromophoric compounds. See heading and footnotes of Fig. 1 [4,6,9,64,72,91,97,107,119–134].

parent nonamethine merocyanine (**77**) and of the simple polyenic push–pull carotenoid (**80**) amounts to about 0.1 eV only. The transition energies of indamine dyes **83**–**85** are likewise well reproduced by TDDFT. These dyes are distorted in relation to the planarity. The compound **86** can be considered as a merocycanine. Campaigne et al. studied heterocyclic merocyanines and found systematic deviations. The last square fit reduced the error to 0.09 eV [61]. As similarly reported for CT-type nitrodiphenylamine dyes [62] no substantial error was observed for CT-type merocyanines.

3.3. Assorted chromophoric compounds

The error for the remaining compounds **87–130** is variable (Fig. 3). Whereas the transition energy of **87** is only slightly overestimated a fatal error occured with **89**–**91**. The MAE amounts to 0.57 eV. These compounds are push–pull-substituted *para*-quinodimethanes. Recalculation of **89** with the extended basis set 6-311 + G(2d,p) and consideration of the bulk solvent effect (chloroform) by PCM-TDDFT reduced the excitation energy from 2.69 to 2.40 eV. Thus, the excitation energy remains to be 0.48 eV in error corresponding to 177 nm in wavelengths. Calculations with the approximate TDDFTB method show the same defect [53]. The experimental data of **89**–**91** appear reliable. Closely similar experimental data are mentioned in other studies of **88**. The CT-type dye **89** is of blue color in CH_2Cl_2 displaying a fine structure with absorption maxima at 548 and 641 nm (2.12 and 1.92 eV, respectively) and **90** is a green–black compound of faint yellow color in solution absorbing s in the near infrared with absorption maxima of 957 and 1045 nm (1.30 and 1.19 eV, respectively). The CT-type

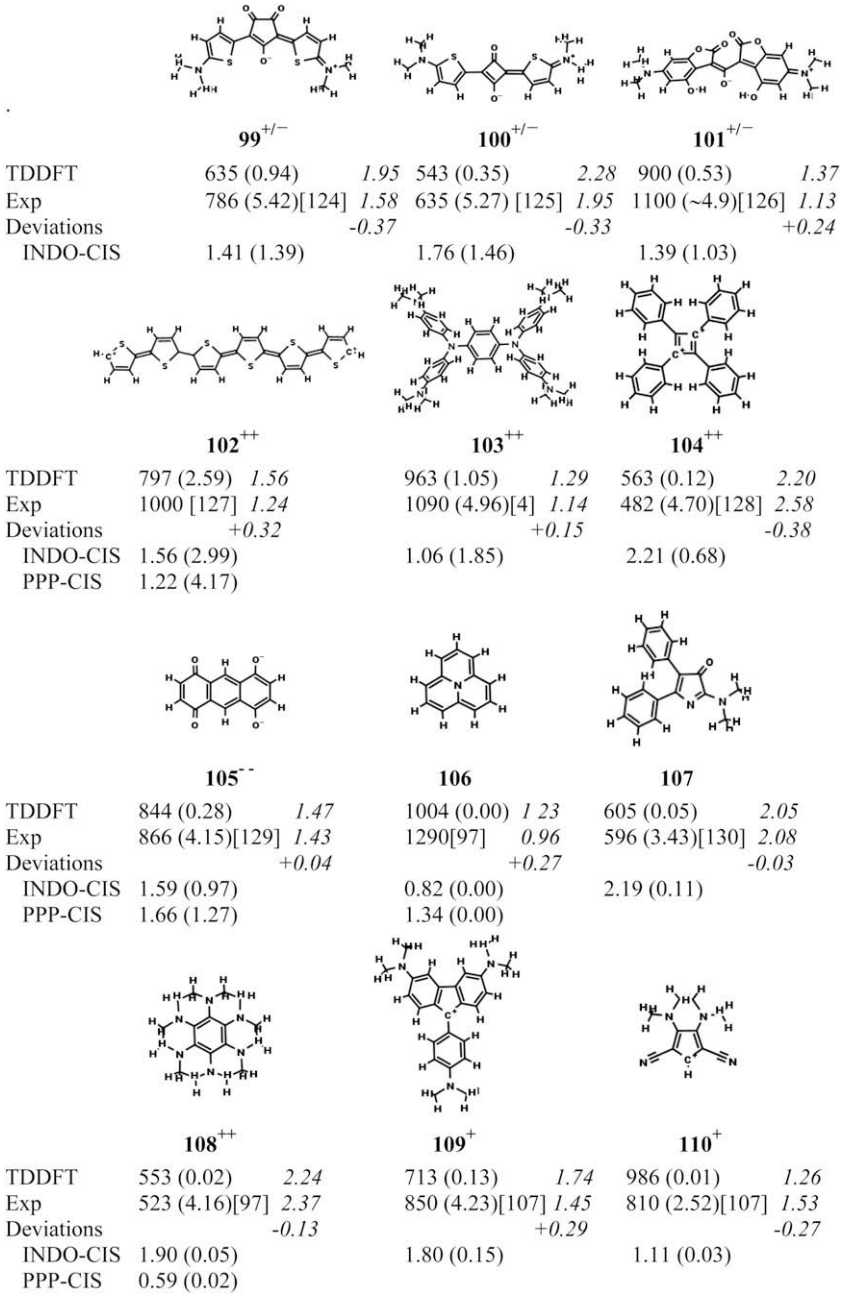


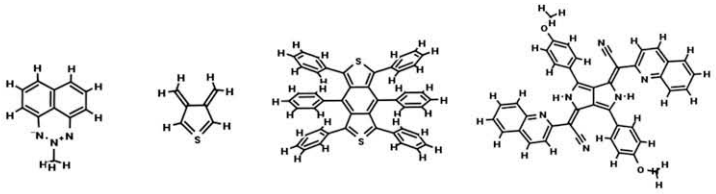
Fig. 3. (*continued*).

quinarene **91** is also considerably in error whereas the simpler compound **92** exhibits a low deviation.

A large charge transfer upon excitation is known for betainic dyes. The spectral data of the prototype betaine dyes **94**$^{+/-}$–**95**$^{+/-}$ measured in non-polar solvents are satisfactorily reproduced. The deviation amounts to about 0.2 eV. Reichardt's dye **95** displays an extremely strong positive solvatochromism [63]. The experimental value of 795 nm measured in dioxane was taken to compare theory and experiment. The excitation energy of 4-pyridiniumphenolate **94**$^{+/-}$ was estimated [64] from experimental value measured in a polar solvent.

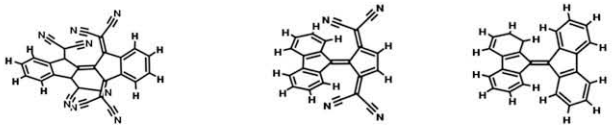
Whereas the deeply colored mesoionic compounds **96**$^{+/-}$ and **97**$^{+/-}$ were accurately calculated the spectral data of the mesoionic croconaine NIR-dyes **98**$^{+/-}$ and **99**$^{+/-}$ and of the squaraine dye **100**$^{+/-}$ are in error by about 0.3 eV. The calculation of **99**$^{+/-}$ and **100**$^{+/-}$ with the same heterocyclic substituent groups, however, correctly predicted croconaine dyes as more bathochromic than squaraine dyes. An overestimation of the transition energies of croconaine and squaraine dyes has been reported by Bhanuprakash et al. [27]. The study of the singlet–triplet gap and the consideration of additional criteria let them to conclude that the croconaine dyes are biradicaloid in nature. Therefore these dyes are not well described by TDDFT that is essentially of single excitation character.

The more recently synthesized NIR absorbing open chain compound **101** is related to the cyclic squaraine and croconaine dyes but its absorption band is about 300 nm red-shifted. This compound belongs to the π,π-biradicaloid dyes ($<S^2>$=0.40). Like the cyclic croconaine compounds the NIR dye **101** contains the hypothetical oxyallyl biradical fragment. *Ab initio* SAC-CI calculations revealed that double excitations actually play an essential role in the



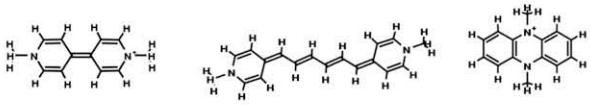
111 **112** **113** **114**

TDDFT	588 (0.02) *2.11*	651 (0.09) *1.90*	756 (0.22) *1.64*	647 (0.89) *1.92*
Exp	607 (2.98)[97] *2.04*	572 (3.71)[9] *2.17*	793 (4.06)[9] *1.56*	731 (4.07) [72] *1.70*
Deviations	*+0.07*	*-0.27*	*+0.08*	*+0.33*
INDO CIS	2.07 (0.0)	1.69 (0.34)	1.15 (0.45)	2.06 (1.11)
PPP-CIS	2.39 (0.48)			



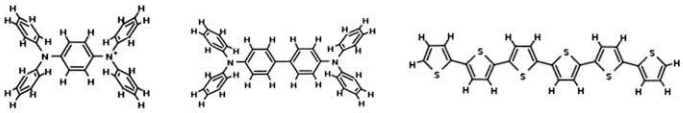
115 **116** **117**

TDDFT	574 (0.13) *2.16*	581 (0.16) *2.13*	479 (0.47) *2.59*
Exp	510[91] *2.43*	650[91] *1.91*	460 (4.34)[97] *2.70*
Deviations	*-0.27*	*+0.22*	*-0.11*
INDO-CIS	2.74 (0.17)	2.15 (0.22)	2.63 (0.72)



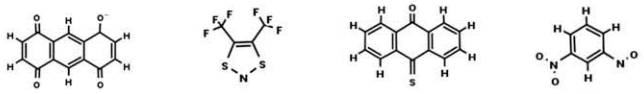
118$^{\bullet+}$ **119**$^{\bullet+}$ **120**$^{\bullet+}$

TDDFT	626 (0.00) *1.98*	908 (0.06) *1.37*	661 (0.02) *1.87*
Exp	605 [131] *2.05*	1075 [132] *1.15*	719 (3.21)[107] *1.72*
Deviations	*-0.07*	*+0.22*	*+0.15*



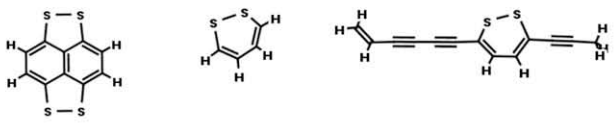
121$^{\bullet+}$ **122**$^{\bullet+}$ **123**$^{\bullet+}$

TDDFT	832 (0.40) *1.49*	1332 (0.65) *1.01*	1325(0.42) *0.94*
Exp	820 [107] *1.51*	1240 (~4.5)[107] *1.24*	1240[127] *0.98*
Deviations	*-0.02*	*-0.23*	*-0.04*



124$^{\bullet-}$ **125**$^{\bullet}$ **126** **127**

TDDFT	1211 (0.13) *1.02*	613 (<0.01) *2.02*	726 (0.00) *1.71*	840 (<0.01) *1.48*
Exp	1560 (4.21) [129] *0.79*	738 (2.41)[4] *1.68*	697 (1.67) [9] *1.78*	760[133] *1.63*
Deviations	*+0.23*	*+0.34*	*-0.07*	*-0.15*



128 **129** **130**

TDDFT	625 (0.00) *1.98*	524 (<0.01) *2.37*	582 (0.19) *2.13*
Exp	700[4] *1.77*	465 (3.51)[134] *2.75*	490 (3.48)[134] *2.53*
Deviations	*+0.21*	*-0.38*	*-0.40*

Fig. 3. (*continued*).

Table 1
Absorption wavelengths of the lowest-energy transitions in nanometers of streptopolymethine cyanines: $Me_2N–(CH)_n–NMe_2^+$.

Method	*n*						
	1	3	5	7	9	11	13
Time-dependent DFT[a]							
B3LYP/6-31 + G(d)	204	264	330	390	443	499	551
B3LYP/6-311 + G(d,p)	206	266	332	391	445	501	553
B3LYP/6-311 + G(3df,p)	207	267	333	393	446	502	554
B3LYP/aug-cc-pVTZ	208	267	333	–	–	–	–
PBE0/6-311 + G(d,p)	203	263	329	389	442	498	550
BLYP/6-311 + G(d,p)	217	275	340	399	436	507	554
BHandHLYP/6-311 + G(d,p)	170	255	321	381	436	492	545
TDDFT/TDA[a,b]	192	241	293	337	376	418	–
TDDFTB[c]	213	280	348	409	467	522	575
Ab initio							
RHF[a]	170	225	284	337	386	435	481
SCS-CIS(D)[d]	220	303	411	526	647	776	–
SAC-CI[e]	210	292	411	571	–	–	–
SORCI[f]	204	282	371	460	546	642	728
CASPT2[g]	187	284	385	484	585	–	–
Calculated from linear correlations							
B3LYP/6-311+G (d,p)[a]	205	312	430	536	633	738	826
$1/\Delta\epsilon$ (DFT)[a]	213	313	424	530	629	731	840
$1/\Delta x$ (HMO)[a]	214	317	420	525	630	735	839
Semi-empirical approaches							
PPP[h]	221	317	408	497	595	627	761
PPP "new γ"[i]	226	318	420	522	623	724	823
INDO-CIS[j,m]	260	334	414	489	561	625	687
INDO-RPA[j,m]	273	353	439	519	594	664	730
AM1-CIS [k,m]	227	347	431	517	602	684	759
PM3-CIS[k,m]	309	372	456	541	627	710	787
Experimental data[n]							
in CH_2Cl_2	224	313	416	519	625	735	848

[a] This study, B3LYP/6-31 + G* optimum geometries [34].
[b] This study, 6-31G [38].
[c] [19,53].
[d] [83].
[e] This study, SAC-CI/6-31G*,Level 2 [36];
[f] This study, 6-31G [37].
[g] [28].
[h] [84].
[i] Full CIS [85].
[j] [86].
[k] This study CIS (10 × 10); results with two extended configuration interactions, *n* = 9: AM1-CISD (18,18):572 nm and AM1-CAS (18,18): 558 nm [87].
[m] AM1 optimum geometries.
[n] [88].

lowest-energy transitions [27]. According the TDDFT calculation the error in the case of **101** is comparable with that of the related croconaine dyes. Replacement of 6-31 + G* by 6-311 + G(2d,p) shifts the transition energy closer to the experiment by 0.25 eV. In the sensitive wavelength scale the calculated wavelengths of 900 nm corresponds to 1100 nm in experiment. SAC-CI calculations predicted the absorption of **101** at shorter wavelengths at 716 nm.

The compounds **102**–**105** are doubly charged. In two of four cases the transition energies are markedly overestimated. The transitions energies calculated for the long-wave absorbing oligothiophene dications are too large [65]. These compounds are again biradicaloid. However, according to the BS-TDDFT calculations the $<S^2>$ value of the quinquethiophene dication **102** amounts to only 0.18.

The following compounds comprise potential anti-aromatic ring structures (**106**–**110**) and non-Kekulé-type structures (**111**–**113**). Additionally these structures are considerably twisted around an essential double bond (**115**–**117**). The neutral cycl[3.3.3]azine (**106**) with a bridged antiaromatic 12π perimeter exhibits a low-lying electronically excited state giving rise to an absorption maximum at 1290 nm (cf. Fig. 3). In agreement with the experiment an electronic transition was calculated at about 100 nm lower wavelengths in the NIR region. The compounds **107**–**110** contain a local ring system which is related to monocylic antiaromatic 5- or 6-membered rings with 4π electrons. Using the nucleus-independent chemical shift (NICS) at the centre of the ring as a diagnostic probe of the magnetic shielding [66] the antiaromatic character of these compounds is indicated by positive values of NICS. The value is relatively large for **108** (+29.2 ppm) and less for **107**, **109** and **110** (about +10 ppm). The transition energies of the NIR absorbing species **105** and **106** are surprisingly well reproduced. The blue heterocycle **111** belongs to the N-ylids and is a non-Kekulé-type structures. A biradical formula is suggested alternatively to the ylidic formula presented in Fig. 3. However, the biradical character was not verified by the BS-DFT calculation.

The calculated weak electronic transition of 3,4-dimethylenethiophene (**112**) obviously corresponds to the experimentally observed absorption maximum at 572 nm [67]. The non-Kekulé-type heterocycle is a derivative from the well-studied disjoint singlet biradical tetramethyleneethene (TME). Sulfur replaces two hydrogen atoms of TME. For simplicity the $\lambda^4\sigma^2$ tetravalent formula of **112** [68] is presented in Fig. 3. According to previous studies compounds of this structure are a biradicaloid singlet compounds with a low singlet–triplet gap [68–70]. In agreement the BS-UDFT calculation **112** revealed singlet–triplet instability. The $<S^2>$ value is relatively large (0.72 without and 0.92 with geometry optimization). The TDDFT calculation resulted in the transition energy 1.9 eV to compare with 2.17 eV measured by cold matrix isolation technique. Because TDDFT is essentially a single-configurational approach, a strong error was expected. An implicit coverage of multi-reference effects by DFT [71] may explain the reasonable prediction. Because of the strong biradical character of **112**, simplified multiconfigurational *ab initio* calculations were performed by the SORCI method [37] using Gaussian- and Dunning-type basis sets. The calculations resulted in 2.21 eV with 6-31 + G* and 2.03 eV with aug-cc-pVDZ basis sets. Thus the transition energies calculated by SORCI are close to the experimental finding. The hexaphenyl-substituted sulfur heterocycle **113** is a derivate of the disjoint 1,2,4,5-tetramethylenebenzene biradical. This non-classical compound **113** and the more recently prepared compound **114** [72] of classical structure absorb at more than 700 nm. The transition energies of these relatively large compounds are well calculated.

The orange to blue colored compounds **115–117** are heavily twisted around the double bond for steric reasons. The mostly distorted structure is **115** with a twist angle of 49.7° and is expected to be slightly biradicaloid ($<S^2> = 0.18$). Nevertheless, the deviation of the calculated transition energy from the experimentally determined value is surprisingly low with 0.13 eV, on average.

Less is known about the TDDFT calculations of spectral absorptions of dye radicals. The results of the lowest-energy transitions of the radicals **118**$^{\bullet+}$**–124**$^{\bullet+}$ were promising. The long-wavelength absorptions of the radicals are due to $\pi \rightarrow \pi^*$ transitions. The electrochemically generated Weitz-type radicals **118**$^{\bullet+}$**–120**$^{\bullet+}$ are predicted to absorb weakly at long wavelengths whereas the Wurster-type radicals **121**$^{\bullet+}$**–124**$^{\bullet+}$ are intensively absorbing in NIR. These experimental findings are well reproduced. Piccard early assumed that colored compounds prepared by oxidation of benzidine diamines led to NIR dyes when extending the chain. The observed change of color was due to the red-shift of the shorter wavelength absorption band ("color of higher orders") [73]. As was subsequently revealed experimentally Piccard's dye salts contain radical cations, such as the blue **117**$^{\bullet+}$. The neutral dithiazolyl radical **125**$^{\bullet}$ is a black–green liquid displaying a weak absorption band near 730 nm. The calculated $\pi \rightarrow \pi^*$ transition energy is overestimated by 0.34 eV. Extension of the basis set had only a minor effect on the result.

The color of the compounds **126–128** absorbing at long wavelengths is due to non-$\pi \rightarrow \pi^*$ transitions of relatively weak in intensity. The first two repesentatives exhibit $n\pi^*$ ($\sigma\pi^*$) chromphores. The theoretical results are satisfactory. The color determining weak lowest-energy absorptions of thiocarbonyl [74] nitroso [75] and azo compounds [76] were extensively studied by Jacquemin et al. The experimental data are generally very well reproduced in these studies. The weak absorptions of the cyclic-conjugated disulfide **128** and **129** are of the $\pi \rightarrow \sigma^*$-type [9,77]. In the case of the tetrasulfide **123** the transition is dipole forbidden but allowed in the folded yellow-orange 1.2-dithiin (**129**). The electronic transition of the red natural dye thiarubrine (**130**), however, exhibit both the characteristics of the $\pi \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transition.

Many of the colored compounds considered in this section are less well characterized than conventional dyes and information about the structure are rare to check the calculated geometries. Uncertainty in the structure will contribute to the deviations. However, the large number of compared data should provide realistic conclusion about strength and limitation of the TDDFT method and inspire confidence on the method in the scope of applicability. The mean absolute deviation of the heterogeneous series of dyes **74**–**130** of structure including three cases considerably in error (**89**–**90**) amounts to 0.21 eV (57 data) and is therefore larger the deviation of the more homogeneous series **1–41** (0.15).

3.4. Comparative calculations at semi-empirical levels

In many cases semi-empirical calculations are informative. For comparison, semi-empirical calculations at the INDO-CIS all-valence electron and PPP π-level were executed. The results were added to the Figs. 1–3. DFT-optimized molecular geometries were used in all these calculations. Since parameters of boron are not yet contained in the INDO-CIS program, transition energies of the compounds **71–73** are missing. The parent cyanines are reasonably well calculated. The results of the INDO-CIS calculations were clearly inferior to TDDFT results (MAE = 0.29 eV, 110 data). In thecase of indigoid dyes **31–38** the method fails seriously (MAE = 0.83 eV, 8 data). These dyes were excluded from the forementioned statistics. In the case of disulfides the failure of INDO-CIS is due to the fact that $\pi \rightarrow \sigma^*$- type transitions are not calculated in the visible region. This failure was discussed elsewhere for the 1,2-dithiin parent compound (**129**) [9].

In contrast to TDDFT and INDO-CIS the PPP method works reasonably well for all dyes with planar conjugated system. The error (MAE = 0.24, 63 data) is somewhat larger than the error in the previous study (0.20 eV [9]). The present study included very different structures that need a larger number of heteroatomic parameters. The results of the PPP calculations with the "new γ"-approximation are in excellent agreement with the experimental data (cf. Table 1). The theoretical and experimental absorption wavelengths differ for the monomethine (in the near UV absorption) by 3 nm (0.04 eV) and for tridecamethine (near infrared absorption) by 25 nm (0.05 teV).

Finally it should be mentioned again that the popular fitting methods plotting theoretical against experimental absorption wavelengths within related dyes series allow favorably good presentation of the results (see Table 1). In the case of the Hückel MO method the plot of the inverse HOMO-LUMO gaps $1/\Delta x \times ß^{-1}$ against the experimental data provided accurate absorption wavelengths and "vinylene shifts" of about 100 nm in going from one to next vinylogue (Table 1). Furthermore, the inverted Kohn–Sham orbital energies $1/\Delta\epsilon$ (DFT) and the erroneous calculated absorption wavelengths of streptocyanines plotted versus the experimental data resulted in a close correlation (B3LYP/6-311 + G (d,p) approximation). The absorption wavelengths calculated from the linear correlations agree well with the experimental results (Table 1). Thus the error between TDDFT transition energies and experimental excitation energies is systematic.

4. Discussion

A unexpected finding of this study is the fact that TDDFT works satisfactorily well in cases where it was not expected but failed in seemingly trivial cases. Examples of the first kind are biradicaloid compounds and of the second kind are cationic and anionic polymethine dyes. The transition energies of most simple cyanines and oxonols and of many more complex derivatives are strongly overestimated. A few erroneous cases were also encountered among charge-transfer-type compounds which undergo a characteristic transfer of charge upon excitation.

Some drawbacks of TDDFT are already known [78,79]. The presently used functionals suffer from "short-sightness" because of the short-range behaviour of the hybrid functionals. Functionals were developed to take into account long-range effects (DFT-LR-functionals [80]). However this error concern polymers and large aggregated compounds and is not relative to small dye molecules. Calculations on streptopolymethine cyanines with long-range functionals did actually not solve this problem [28,80]. Another critical aspect concerns the neglect of higher-excited states. However, *ab initio* CASPT2 calculations of streptopolymethine cyanines revealed that the second excited state but not the first color-determining exited state has multiconfigurational character [28]. Promising approaches for future studies of the electron excitation of polymethines are the DFT-based multireference configuration interaction (DFT/MRCI) [81,82]) and the simplified multirefernce *ab initio* method SORCI.

5. Summary

Time-dependent density functional theory calculations on spectral excitation of numerous colored compounds of different charge and multiplicity and of quite different structure unveiled the scope and limitation of the method. In general, the performance of the method is very satisfying (MAE = 0.18 eV, 102 data), however, calculated transition energies of cationic cyanines, of anionic oxonols and various related dyes are much too high (MAE = 0.52 eV, 32 data) and the absorption wavelengths are correspondingly too low. Refinement of the theoretical model and consideration of the solvent effect did not basically improve the results in erratic cases. The transition energies of cationic hemicyanines, neutral merocyanines and push-pull polyenes are well predicted. Caution is advisable in the case of push-pull-substituted quinoid CT-type dyes although only three cases were found to be strongly in error. Broken-symmetry UDFT calculations revealed the biradical character of some quinoid compounds derived from p-quinodimethane and of some non-Kekulé-type structures. Unexpectedly the calculated excitation energies of compounds of biradicaloid or antiaromatic character were not much more in error than those of conventional dyes. Calculations of dye radicals were also promising.

If the limitations are considered the TDDFT method favorably enriches the arsenal of theoretical methods in estimating the position of spectral absorptions. The results of the TDDFT calculations of dyes proved to be clearly superior to those of semi-empirical INDO-CIS and PPP calculations.

Acknowledgments

I am very grateful to H. Hartmann (Dresden) for support, advice, and information about more recent development in dye chemistry.

H.-U. Wagner (München) put kindly at disposal an improved and extended version of the PPP-program. I thank G. Seifert (Dresden) for discussions and for TDDFTB test calculations. Results of AM1-CI calculations were kindly made available by N. Drebov (Sofia). I am indebted to E. Lewars (Peterborough/Canada) for comments to the manuscript.

References

[1] Zollinger H. Color chemistry. In: Syntheses, properties, and applications of organic dyes and pigments. 3rd revised ed.. Zürich: Verlag Helvetica Chimia Acta, Wiley VCH; 2003.
[2] Kim S- H. Functional dyes. Amsterdam: Elsevier; 2006.
[3] Dähne S, Rensch-Genger U, Wolfbeis OS, editors. Near-infrared dyes for high technology applications (NATO Series 3). Dortrecht: Kluwer Academic Publishers; 1994.
[4] Fabian J, Nakazumi H, Matsuoka M. Near-infrared absorbing dyes. Chem Rev 1992;92:1197–226 [and references therein].
[5] Griffith J. Colour and constitution of organic molecules. London: Academic Press; 1976.
[6] Fabian J, Hartmann H. Light absorption of organic colorants. Theoretical treatment and empirical rules. Berlin: Springer; 1980 [and references therein].
[7] Griffiths J. Recent developments in the color and constitution of organic dyes. Rev Progr Color Rel Top 1981;11:37–57.
[8] Griffiths J. Practical aspects of color prediction of organic dye molecules. Dyes Pigments 1982;3:211–33.
[9] Fabian J. Electronic excitation of sulphur-organic compounds – performance of the time-dependent density functional theory. Theor Chem Acc 2001;106:163–236.
[10] Nishimoto K. A MO theoretical study of organic dyes I. Effect of chemical softness on the electronic spectra. Bull Chem Soc 1993;66:1876–80.
[11] Tachikawa T, Hiruta K, Tokita S, Nishimoto K. PPP calculations for electronic spectra of cyanine dyes, part 2. J Photopolym Sci Techn 2000;13:183–6.
[12] Zerner MC. Semiempirical molecular orbital methods. In: Lipkowitz KB, Larter R, Cunsari Th R, editors. Rev Comp Chem, 2; 1991. p. 313–65. New Jersey:Wiley VCH; 2004, p. 153–218 [and references therein].
[13] Tretiak S. Random phase approximation/semiempirical computations of electronic structure of extended organic molecules. Recent Research Developments in Physical Chemistry 2001;5:721–45.
[14] Matsuura A, Sato H, Sutoyama W, Takahashi A, Sakurai M. AM1, PM3 and PM5 calculations on the absorption maxima of basic organic dyes. J Mol Struct Theochem 2008;860:119–27.
[15] Kawauchi S, Muta H, Satoh M, Komiyama J, Watanabe J, Tamura Y, et al. AM1-RPA calculation for predicting UV-visible spectra of some dyes. Nonlin Opt 2000;26:221–8.
[16] Adachi M, Nakamura S. Comparison of the INDO/S and the CNDO/S method for the absorption wavelength calculation of organic dyes. Dyes Pigments 1991;17:287–96.
[17] Guillaumont D, Nakamura S. Calculation of the absorption wavelengths of dyes using time-dependent density functional theory (TD-DFT). Dyes Pigments 2000;46:83–92.
[18] Koch W, Holthausen MC. A chemist's guide to density functional theory. Weinheim: Wiley, VCH; 2000 [and references therein].
[19] Niehaus TA, Suhai S, Della Sala F, Lugli P, Elstner M, Seifert G, et al. Tight binding approach to time-dependent density-functional response theory. Phys Rev.B 2001;63:085108.
[20] Wanko M, Garavelli M, Bernardi F, Frauenheim T, Elstner M. A global investigation of excited state surfaces within time-dependent density-functional response theory. J Chem Phys 2004;1674:1674–92.
[21] (a) Sundholm D. Density functional theory calculations of the visible of chlorophyll *a*. Chem. Phys Lett 1999;302:480–4;
(b) Interpretation of the electronic absorption spectrum of free-base porphin using density functional theory. Phys Chem Phys 2000;2:2275–81;
(c) A density-functional.theory study of bacteriochlorphyll *b*. Phys Chem Phys 2003;5:4265–71;
(d) Comparison of the electronic excitation of chlorophyll a and pheophytin calculated at density functional theory level. Chem Phys Lett 2000;317:545–52.
[22] Parusel ABJ, Grimme St. DFT-MRCI calculations on the excited states of porphyrin, hydroporhyrins, tetraazaporhyrins and metalloporphyrins. J. Porph Phthal 2001;5:1–8.
[23] (a) Jacquemin D, Preat J, Wathelet V, Perpète EA. Substitution and chemical environment effect on the absorption spectrum of indigo. J Chem Phys 2006;124(074104):1–12;
(b) Perpète EA, Preat J, André J-M, Jacquemin D. An ab initio study of the absorption spectra of indirubin, isoindigo and related derivatives. J Phys Chem A 2006;110:5629–35.
[24] (a) Jacquemin D, Preat J, Wathelet V, Fontaine M, Perpète EA. Thioindigo dyes: highly accurate visible spectra with TD-DFT. J Am Chem Soc 2006;128:2072–83;
(b) Jacquemin D, Preat J, Wathelet V, Perpète EA. Theoretical investigation of the absorption spectrum of thioindigo dyes. J Mol Struct Theochem 2005;731:67–72;
(c) Perpète EA. Jacquemin D. TD-DFT benchmark for indigoid dyes. J Mol Struct Theochem; in press.
[25] (a) Jacquemin D, Preat J, Wathelet V, Perpète EA. Time-dependent density functional theory determination of the absorption spectra of naphthoquinones. Chem Phys 2006;328:324–32;
(b) Perpète EA, Lambert C, Wathelet V, Preat J, Jacquemin D. Ab initio studies of the λ_{max} of naphthoquinone dyes. Spectrochim Acta A 2007;68:1326–33.
[26] (a) Jacquemin D, Assfield X. 116:6549; 2002. (b) Jacquemin D, Preat J, Charlot M, Wathelet V, André JM, Perpète EA. Theoretical investigation of substituted anthraquinone dyes. J Chem Phys 2004;121:1736–42;
(c) Perpete EA, Wathelet V, Preat J, Lambert C, Jacquemine D. Toward a theoretical quantitative estimation of the λ_{max} of anthraquinone-based dyes. J Chem Theor Comput 2006;2:434–40;
(d) Jacquemin D, Wathelet V, Preat J, Perpete EA. *Ab initio* tools for the accurate prediction of the visible spectra of anthraquinones. Spectrochim Acta A 2007;67A:334–41;
(e) Perpete EA, Wathelet V, Preat J, Lambert C, Jacquemine D, Perpète EA. Comparison of theoretical approaches for predicting the UV/Vis spectra of anthraquinones. Mol Phys 2007;105:325–31;
(f) Jacquemin D, Perpéte EA, Ciofini I, Adamo C. Accurate simulation of optical properties in dyes. Acc Chem Res 2009;42:326–34.
[27] (a) Prabhakar Ch, Yesudas K, Chaitanya GK, Sitha S, Bhanuprakash K, Rao VJ. Near infrared absorption in symmetric squarylium and croconate dyes: a comparative study using symmetry-adapted cluster-configuration interaction methods. J Phys Chem A 2005;109:8604–16;
(b) Yesudas K, Chaitanya GK, Prabhakar Ch, Bhanuprakash K, Rao VJ. Structure. bonding, and lowest energy transitions in unsymmetrical squaraines. A computational study. J Phys Chem 2006;110:11,717–11,729;
(c) Prabhakar Ch, Chatanya GK, Sitha S, Bhanuprakash K, Rao VJ. Role of the oxyallyl substructure in the near infrared (NIR) absorption in symmetrical dye derivatives: a computational study. J Phys Chem A 2005; 109:2614–22;
(d) Srinivas K, Prabhakar Ch, Devi CL, Yesudas K, Bhanuprakash K, Rao VJ. Enhanced diradical nature in oxyallyl derivatives leads to near infrared absorption: a comparative study of the squaraine and croconate dyes using computational techniques. J Phys Chem A 2007;111:3378–86;
(e) Thomas A, Srinavas K, Prabhakar Ch, Bhanuprakash, Rao JV. Estimation of the first excitation energy in diradicaloid croconate dyes having absorption in the near infrared (NIR). Chem Phys Lett 2008;454:36–41.
[28] Schreiber M, Buß V, Fülscher MP. Electronic spectra of symmetric cyanine dyes: a CASPT2 study. Phys Chem Phys 2001;3:3906–12.
[29] Champagne B, Guillaume M, Zutterman F. TDDFT investigation of the properties of cyanine dyes. Chem Phys Lett 2006;425:105–9.
[30] (a) Grimme St, Parac M. Substantial errors from time-dependent density functional theory for the calculations of excited states of large π systems. Chem Phys Chem 2003;4:293–5;
(b) Parac M, Grimme St. A TDDFT study of the lowest excitation energies of polycyclic aromatic hydrocarbons. Chem Phys 2003;292:11–21.
[31] Gräfenstein J, Cremer D. On the diagnostic value of $<S^2>$ in Kohn–Sham density functional theory. Mol Phys 2001;99:981–9.
[32] Kubo T, Sakamoto M, Nakasuji K. Biradicaloid character of phenalenyl-based aromatic compounds with small HOMO–LOMO gap. Polyhedron 2005;24:2522–7.
[33] Flynn CR, Michl J. pi, pi-Biradicaloid hydrocarbons. *o*-Xylylene. Photochemical preparation from 1,4-dihydrophthalazine in rigid glass, electric spectroscopy, and calculations. J Am Chem Soc 1974;96:3280–8.
[34] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheesman JR, et al. Gaussian 03, revision C.02. Wallingford, CT: Gaussian, Inc.; 2004.
[35] Wagner H-U, Fabian J. PPP singlet-CI program WPSIN5f, version 2007.03. TU, Dresden: Univ München; 2007.
[36] Nakajima T, Nakatsuji H. Analytical energy gradient of the ground, excited, ionized and electron-attached states calculated by the SAC/SAC-CI method. Chem Phys Lett 1997;280:79–84.
[37] Neese F. A spectroscopy oriented configuration interaction procedure. J Chem Phys 2003;119:9428–43.
[38] Neese F. A spectroscopy oriented configuration interaction procedure. J Chem Phys 2003;119:9428–43.
[39] Wannere CS, Sattelmeyer KW, Schaefer III HF, von Ragué Schleyer P. Aromaticity: The alternating C–C bond length structures of [14]-, [18]-, and [22] Annulene. Angew Chem Int Ed 2004;43:4200–6.
[40] Hsu C-P, Hirata S. Head-Gordon. Excitation energies from time-dependent density functional theory for linear polyene oligomers: butadiene to dodeacpentaene. J Phys Chem A 2001;105:451–8.
[41] Cappelini G, Malloci, Mulas G. Electronic excitations of oligoacenes: a time dependent density functional theory study. Superlattices Microstructures, 2009;46:14–8.
[42] Michl J, Thulstrup EW. Why is azulene blue and anthracene white? A simple MO picture. Tetrahedron 1976;32:205–9.
[43] Rieger C, Würthner F. Core-tetrasubstituted naphthalene diimides: synthesis, optical properties, and redox characteristics. J Org Chem 2007;72:8070–2.
[44] Miao L, Yao Y, Yang F, Wang Z, Li W, Hu J. A TDDFT and PCM-TDDFT studies on absorption spectra of *N*-substituted 1,8-naphtylamide dyes. J Mol Struct Theochem 2008;865:79–87.
[45] Savkoa M, Kaščáková S, Gbura P, Miškovský P, Uličný J. Performance of time dependent density functional theory on excitations of medium sized

molecules – test on ionic forms of anthraquinone dihydroxy derivatives. J Mol Struct Theochem 2007;823:78–86.
[46] Montgomery LK, Huffman JC, Jurczak EA, Grendze MP. The molecular structures of Thiele's and Chichibabin's hydrocarbons. J Am Chem Soc 1986;108:6004–11.
[47] Kikuchi A, Iwahori F, Abe J. Definitive evidence for the contribution of biradical character in a 1,4-(4,5-diphenylimidazol-2-ylidene)cyclohexa-2,5-diene. J Am Chem Soc 2004;126:6526–7.
[48] Kikuchi A, Iwahori F, Abe J. Electronic structure of π-conjugated delocalized biradicals. Polym Prepr Jpn 2006;55:1396.
[49] Takahashi T, Matsuoka K-I, Takimiya K, Otsubo T, Aso Y. Extensive quinoidal oligothiophenes with dinitrilomethylene groups at terminal positions as highly amphoteric redox molecules. J Am Chem Soc 2005;127:8928–9.
[50] Ortiz RP, Casado J, Hernández, López Navarette JT, Viruela PM, Orti E, Takimya, Ossubo T. On the biradical nature of long quinoidal oligothiophenes: experimental evidence guided by theoretical studies. Angew Chem Int Ed 2007;46:9057–61.
[51] Abbott LC, Batchelor SN, Oakes J, Lindsay Smith JR, Moore JN. Semi-emprical and ab initio studies of the structure and spectroscopy of the azo dye direct blue: comparison with experiment. J Phys Chem A 2004;108: 10,208–10,218.
[52] Chen PC, Chieh YC, Wu JC. Theoretical Study of the electronic spectra of azo benzene dyes. J Molec Struct Theochem 2005;715:183–9.
[53] Seifert G, Luschtinetz R. Private communication; 2009.
[54] Grimme St, Neese F. Double hybrid density functional theory for excited electronic states of molecules. J Chem Phys 2008;127:154118/1–18.
[55] Wang LY, Chen QW, Zhai GH, Wen ZY, Zhang ZX. Investigation of the structure and absorption spectra for some hemicyanine dyes with pyridine nucleus by TD-DFT/PCM approach. J Mol Struct Theochem 2006;778:15–22 [and references therein].
[56] Bertolino CA, Ferrari AM, Barolo C, Viscardi G, Caputo G, Coluccia S. Solvent effect on indocyanine: a computational approach. Chem Phys 2006;330: 52–9.
[57] Guillaume M, Liégeois VNB, Zutterman F. Time-dependent density functional theory investigation of the absorption and emission spectra of a cyanine dye. Chem Phys Lett 2007;446:165–9.
[58] Loudet A, Burgess K. BODIPY dyes and their derivatives: synthesis and spectrospic properties. Chem Rev 2007;107:4891–932.
[59] Prieto JB, Arbeloa FL, Martinez VM, Lopez TA, Arbeloa IL. Structural and spectroscopic characteristics of pyrromethene 567 laser dye. A theoretical approach. Chem Phys Chem 2004;6:4247–53.
[60] Quartarolo AD, Russo N, Sicilia E. Structures and electronic absorption spectra of a recently synthesized class photodynamic therapy agents. Chem Eur J 2006;12:6797–803.
[61] Guillaume M, Champagne B, Zutterman F. Investigation of the UV/Visible absorption spectra of merocyanine dyes using time-dependent density functional theory. J Phys Chem 2006;110:13007–13.
[62] Jacquemin D, Bouhy M, Perpète EA. Excitation spectra of nitro-diphenylaniline: accurate time-dependent density functional theory predictions for charge transfer dyes. J Chem Phys 2006;204321:1–9.
[63] (a) Reichardt Ch. In: Solvents and solvent effects in organic chemistry. 3rd ed. Weinheim: Wiley; 2004;
(b) Pyridium-*N*-phenolate betaine dyes as empirical indicators of solvent polarity: some new findings. Pure Appl Chem 2008;80:1415–32.
[64] Diemer V, Chaumeil H, Defoin A, Jacques P, Carré Ch. Synthesis of 4-[*N*-methyl-4-pyridino]-phenolate (POMP) and negative solvatochromism of the model molecule in view of nonlinear optical applications. Tetrahed Lett 2005;46:4737–40.
[65] Fabian J, Hartmann H. Chromophores of neutral and dicationic thiophene-based oligomers – a study by first-principles methods. Dyes Pigments 2008;79:126–39.
[66] Von Ragué Schleyer P, Maerker C, Dransfeld A, Jiao H, van Eikema Hommes NJR. Nucleus-independent chemical shifts: a simple and efficient aromatic probe. J Am Chem Soc 1996;118:6317–8.
[67] Greenberg MM, Blackstock SC, Stone KJ, Berson JA. Ground-state multiplicities of 3,4-dimethehylenefuran and dimethylenethiophen. Experimental tests of ab initio and semiempirical theories of heteroatom-bridged disjount biradials. J Am Chem Soc 1989;111:3671–779.
[68] Fabian J, Hess Jr BA. $\lambda^4\sigma^2$-Sulfur heterocycles. An ab initio and density functional study. J Org Chem 1997;62:1766–74.
[69] Tukada H, Bangal PR, Tamai N, Yokoyama Y. Hetero-atom stabilization of zwitterionic non-Kekulé molecules: a DFT study on energy gap between zwitterionic singlet and bradical triplet states. J Mol Struct Theochem 2005;724:215–9.
[70] Du P, Hrovat DA, Borden WT. Ab initio calculations of the singlet–triplet energy separation in 3,4-dimethylenenefuran and related diradicals. J Am Chem Soc 1984;108:8086–7.
[71] Cremer D, Filatov M, Polo V, Kraka E, Shaik S. Implicit and explicit coverage of multi-reference effects by density functional theory. Int J Mol Sci 2002;3:604–38.
[72] Fischer GM, Ehlers AP, Zumbusch A, Daltrozzo E. Near-infrared dyes and fluorophores based on diketopyrrolopyrroles. Angew Chem Int Ed 2007;46:3750–3.
[73] Piccard J. Über Farben 2.Ordnung und über holo- und merichinoide Salze. Ber Dtsch Chem Ges 1913;46:1843–60.
[74] (a) Jaquemin D, Wathelet V, Perpete EA. Ab initio investigation of the n → π* transition in thiocarbonyl dyes. J Phys Chem A 2006;110:9145–52;
(b) Preat J, Jacquemin D, Perpète EA. Taylering standard TDDFT approaches for computing UV/Vis transitions in thiocarbonyl chromophores. Int J Quant Chem 2008;108:762–73;
(c) Preat J, Jacquemin D, Vercauteren DP, Perpète EA. A quantitative prediction of the electronic spectra of thiocarbonyl chromophores: DT-DFT versus SAC-CI. Theo Chem Acc 2008;119:463–8.
[75] Jacquemin D, Perpète EA. The n → π* transition in nitroso compounds: a TD-DFT study. Chem Phys Lett 2006;420:529–33.
[76] (a) Jacquemin D, Perpète EA, Ciofini I, Adamo C. On the TD-DFT UV/vis spectra accuracy: the azoalkanes. Theor Chem Acc 2008;20:405–10;
(b) Jacquemin D, Perpète EA, Scuseria GE, Ciofini I, Adamo C. Extensive TD-DFT investigation of the first electronic transition in substituted azobenzenes. Chem Phys Lett 2008;465:226–9.
[77] Fabian J, Mann M, Petiau M. The origin of the color of 1,2-dithiin – interpretation by Kohn–Sham orbitals. J Mol Model 2000;6:177–85.
[78] Magyar RJ, Tretiak S. Dependence of spurious charge-transfer excited states on orbital exchange in TDDFT: large molecules and clusters. J Chem Theory Comput 2007;3:976–87.
[79] Neese F. A critical evaluation of DFT, including time-dependent DFT, applied to bioinorganic chemistry. J Biol Inorg Chem 2006;11:702–11.
[80] Jacquemin D, Perpète EA, Scalmani G, Frisch MJ, Kobayashi R, Adamo C. Assessment of the efficiency of long-range corrected functionals for some properties of large compounds. J Chem Phys 2007;126(144105):1–12.
[81] Grimme St, Waletzke A. Combination of Kohn–Sham density functional theory and multi-reference configuration interaction methods. J Chem Phys 1999;111:5645.
[82] Silva-Junior, Schreiber M, Sauer SPA, Thiel W. Benchmarks for electronically exited states: time-dependent density functional theory and density functional theory based multireference configuration interaction. J Chem Phys 2008;129:104103.
[83] McKelvey, John M, Grimme St., Going beyond conventional TDDFT and CIS predicting UV/Vis properties. Abstracts of papers, 253th ACS national meeting, New Orleans LA, United States; 2008.
[84] Fabian J, Zahradník R. PPP calculations on the vinylene shift of symmetric dyes. Wiss Z TU Dresden 1977;26:315–23.
[85] Wagner HU. Private communication; 2008.
[86] Peichert R. Private communication; 2008.
[87] Drebov N. Private communication; 2008.
[88] Malhotra SS, Whiting MC. The preparation and electronic spectra of homologous series of simple cyanines, merocyanines and oxonols. J Chem Soc 1960:3812–22.
[89] Perkampus H-H. In: UV-VIS atlas of organic compounds. 2nd ed. Weinheim: VCH; 1992.
[90] Karabunarliev St, Gerghel L, Koch K-H, Baumgarten M. Structure and optical absorption of oligorylenes upon doping. Chem Phys 1994;189:53–65.
[91] Hafner K, Hafner-Schneider G, Bauer F. Azuleno[8,8a,1,1-def]heptaene. Angew Chem Int Ed 1968;7:808–9.
[92] Adachi M, Nagao Y. Design of near-infrared dyes based on π-conjugation system extension. Theoretical evaluation of arylimidazole derivatives of perylene chromophore. Chem Mater 1999;11:2107–14.
[93] Quante H, Müllen K. Quaterrylenebis(dicarboxamides). Angew Chem Int Ed 1995;34:1323–5.
[94] Green FJ. The sigma–aldrich handbook of stains, dyes and indicators. Aldrich Chemical Comp Inc.; 1990.
[95] Sugimoto T, Nagatomi T, Ando H, Yoshida Z. Redoxactive thieno[3,2-b]thiophene as a novel three-color electrochromic system. Angew Chem Int Ed 1988;27:560–1.
[96] Wittig G, Dreher E, Reuther W, Weidinger H, Steinmetz R. Über p-xylene. Ein Beitrag zur Valenztautomerie ungesättigter Syteme. Liebigs Ann Chem 1969;726:188–200.
[97] Fabian J, Zahradnik R. The search of highly colored organic compounds. Angew Chem Int Ed 1989;28:677–828 [and references therein].
[98] Kikuchi A, Ito H, Abe J. A new family of π-conjugated delocalized biradicals: electronic structures of 1,4-bis(2,5-diphenylimidazol-4-ylidene)cyclohexa-2,5-diene. J Phys Chem B 2005;109:19,448–19,453.
[99] Casado J, Miller LL, Mann KR, Pappenfus TM, Higuchi H, Ortí E, et al. Quinoid oligothiophenes as electron-donor and electron-acceptor materials. A spectroelectrochemical and theoretical study. J Am Chem Soc 2002;124:12,380–12,388.
[100] Takahashi K, Suzuki T. *p*-Diphenoquinone analogues extended by dihydrothiophenediylidene insertion: a novel amphoteric multistage redox system. J Am Chem Soc 1989;111:5483–5.
[101] Cai X, Burand MW, Newman ChR, da Silva Filho DA, Pappenfus TM, Bader MM, et al. N- and P-channel transport behavior in thin film transistors based on tricyanovinyl-capped oligothiophenes. J Phys Chem B 2006;110:14,590–14,597.
[102] Nihira T, Tarutani S, Takase K, Takahashi K. Synthesis and properties of thienyl and oligothienyl substituted tropylium ions. Heterocycles 1995;41:2169–72.
[103] Franck B, Nonn A. Novel porphyrinoids for chemistry and medicine by biomimetric syntheses. Angew Chem Int Ed 1995;34:1795–811.
[104] Seidel D, Lynch V, Sessler JL. Cyclo[8]pyrrole: a simple-to-make expanded porphin with meso bridges. Angew Chem 2002;41:1422–5.

[105] Gompper R, Beck A, Gessner T, Hartmann K, Heindl D, Polborn K, et al. Dyes based on the cyclopentadienylium chromophore and related compounds. In: DähneRensch-Genger SU, Wolfbeis OS, editors. Near-infrared dyes for high technology applications (NATO series 3). Dortrecht: Kluwer Academic Publishers; 1994.
[106] Paramonov VD, Mostoslavskii, Shevchuk MA. Effect of naphthalene fragment annelation on the absorption spectrum and quantum yield of photoisomerization of perinaphththioindigo. Zh Fiz Khim 1978;52: 2676–7.
[107] Fabian J. Polymethine dyes with light absorption in the near infrared. J Prakt Chem 1991;333:197–222 [and references therein].
[108] Webster S, Padilha LA, Hu H, Przhonska OV, Hagan DJ, Van Stryland EW, Bondar MV, Davydenko IG, Slominsky YL, Kachkovski AD. Structure and linear spectroscopic properties of near IR polymethine dyes. J Lumin 2008;128:1972–6.
[109] Tolmachev AI, Slominskii Yu, Ishchenko AA. New cyanine dyes absorbing in the NIR. In: DähneResch-Genger SU, Wolfbeis OS, editors. Near-infrared dyes for high technology applications. NATO Science Series 3. Dortrecht: Kluwer Academic Publishers; 1994.
[110] Kanitz A, Hartmann H. On the nitrosation of *N*-monosubstituted 1-naphthylamines – formation of *N*-monosubstituted 4-nitroso-1-naphthylamine derivatives and benzocondensed indaminium salts. J Prakt Chem 1996;338:414–9.
[111] Jutz Ch, Voithenleitner F. Substituierte Phenyltropyliumionen. Chem Ber 1963;97:29–48.
[112] Hünig S, Quast H. Neue farbige Systeme. In: Foerst W, editor. Optische Anregung organischer Systeme. Weinheim: Verlag Chemie GmbH; 1966. p. p.184–262.
[113] McDonnell SO, ÓShea DF. Near-infrared sensing properties of dimethylamino-substituted BF2-azadipyrromethenes. Org Lett 2006;8:3493–6.
[114] Halik M, Hartmann H. Synthesis and characterization of a new long-wavelengths-absorbing oxonol dyes from the 2,2-difluoro-1,3,2-dioxaborine type. Chem Eur J 1999;5:2511–7.
[115] Mushkalo IL, Dyadyusha GG, Turova LS, Kornilov MYu. A macrocyclic biscyanine dye. Tetrahedron Lett 1980;21:2977–80.
[116] Blanchard-Desce M, Ledoux I, Lehn J-M, Malthête, Zyss J. Push–pull polyenes and carotenoids: synthesis and non-linear optical properties. J Chem Soc Chem Commun 1988:737–9.
[117] Tokita S, Suziki T, Shimokoshi T, Kogo Y, Kafuku K. Molecular structure and electronic spectrum of organic colorants: molecular orbital approach to indoaniline dyes. J Photopolym Sci Technol 1991;4:41–50.
[118] Scheibe P, Schneider S, Doerr F, Daltrozzo E. Spectroscopic studies on merocyanine I. UV and NMR spectra of malonitrile-substituted vinylogous amides. Ber Bunsen-Gesellschaft 1976;80:630–8.
[119] Inoue S, Aso Y, Otsubo T. Push–pull type of diphenoquionoid chromophores as novel near-infrared dyes. Chem Com 1997:1105–6.
[120] (a) Gompper R, Wagner H-U. Effect of anellation on the color of quinomethides, quinodimethanes and arylcarbonium ions. Tetrahedron Lett 1968: 165–9;
(b) Wagner HU. Absorption maximum measured in chloroform, private communication; 2008.
[121] Mayer R, Fabian J, Viola H, Jakisch L. Synthesis und electronic structure of potentially valence isomeric 1,2-dithiolylium-4-olates. Phosph Sulf 1987;31:109–22.
[122] Barrilier D. Physicochemical properties and structural study of 1,2-dithiolium-4-olate and isothiazolium-4-olate. Phosph Sulf 1980;8:79–85.
[123] Avirah RR, Jyothish K, Ramaiah D. Infrared absorbing croconaine dyes: synthesis and metal ion bindung properties. J Org Chem 2009;73:274–9.
[124] Keil D, Hartmann H, Reichardt Ch. Synthesis and spectroscopic characterization of new NIR absorbing (2-thienyl)- and (4-diakylanminoaryl)-substituted croconic acid dyes. Liebigs Ann Chem 1993:935–9.
[125] Keil D, Hartmann H, Moschny T. Synthesis and characterization of 1,3-bis-(2-dialkylamino-5-thienyl)-substituted squaraines. A novel class of intensively coloured panchromatic dyes. Dyes Pigments 1991;17:19–27.
[126] Tian M, Tatsuura S, Furuki M, Sato Y, Iwas I, Pu LS. Discovery of novel dyes with absorption maxima at 1.1 μm. J Am Chem Soc 2003;125:348–9.
[127] Fichou D, Horowitz G, Xu B, Garnier F. Stoichiometric control of the successive generation of the radical cation and dication of extended alpha-conjugated oligothiophenes: a quantitative model for doped polythiophene. Synth Metals 1990;39:243–59.
[128] Freedman HH, Frantz Jr AM. Tetraphenylcyclobutadiene derivate. V The tetraphenylcyclobutenium dication. J Am Chem Soc 1962;84:4165–7.
[129] Almlöf JE, Feyereisen MW, Jozefiak ThH, Miller LL. Electronic structure and near-infrared spectra of diquinone anion radicals. J Am Chem Soc 1990;112:1206–14.
[130] Eicher Th, Abdesaken F, Franke G, Weber JL. Reaction of cyclopropenones with azomethines. Tetrahedron Lett 1975:3915–8.
[131] Kosower EM, Cotter JL. Stable free radicals II, The reduction of 1-methyl-4-cyanopyridinium ion to methylviologene cation radical. J Am Chem Soc 1964;86:5524–7.
[132] Hünig S, Scheutzow D, Cársky P, Zahradník R. Conjugated radicals IX. Experimental study and the LCI-SCF open shell calculations on the electronic spectra and the redox equilibria of the nitrogen-containing violenes. J Phys Chem 1971;75:335–9.
[133] Nakamoto K, Suzuki K. Direct evidence of the $n \rightarrow \pi^*$ transition of the nitroso absorption. J Chem Phys 1954;20:1971–2.
[134] Block E. Recent advances in the chemistry of 1,2-dithiins. Phosph Sulf Silic 1999;153–154:173–92.