Chapter 9
Electron Structure and Optical Properties of Conjugated Systems in Solutions

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Abstract The review deals with the special type of the organic molecules which contain the collective system of π-electrons; the mobility of the electrons that determines both the electron structure and spectral properties of considered conjugated molecules. The classification of the linear conjugated systems is proposed: polymethine dyes, polyenes, donor-acceptor compounds and the differences between them. It is shown that the high mobility of the collective π-electron shell depends on the type of the conjugated system, chain length, symmetry, molecular constitution of the terminal groups, as well as the electron shell (neutral or charge system). Experimentally, the features of the electron structure of conjugated molecules are observed by spectral methods, especially, in various solvents. It is established that different molecular types show the different sensitivity to the solvent polarity. The work reviews principal results that were obtained by the quantum-chemical and spectral study of the linear conjugated systems.

9.1 Introduction

In the conjugated systems atoms of carbon in the sp^2-hybridization form 3 carbon—carbon σ-bonds while the residual $2p_z$ electrons can generate the collective systems of π-electrons (Fig. 9.1). Such systems form both 1-dimensional π-molecules and branched π-electron systems. According to the Daehne 's triad theory [1–4], the con-

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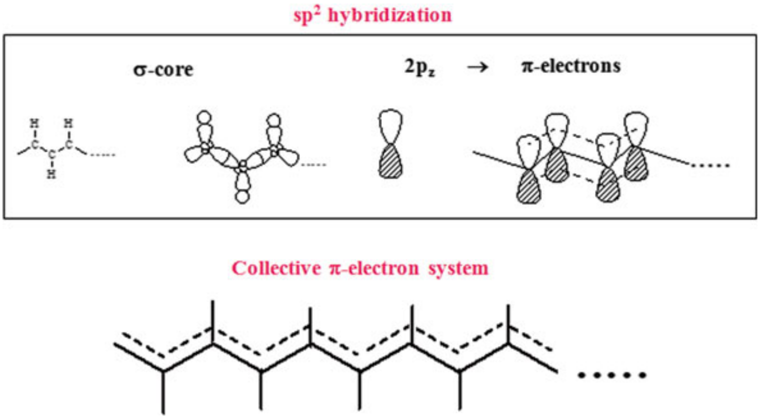


Fig. 9.1 Types of carbon branched π-electron systems

jugated systems are divided on cyclic molecules (or aromatics) and linear molecules (neutral polyenes and ionic polymethine dyes (PMD) as well as their derivatives including the donor-acceptor conjugated molecules).

Collective systems of π-electrons are formed by branched conjugated organic molecules are perspective as functional materials, sensors because of spectral properties (see reviews [5–8] and refers therein). In other hand, the molecules are convenient models for development of new conceptual theoretical approaches that take into consideration the electron properties and chemical topology correctly including both the simplest approaches (based on Hueckel approximation) [9–12] and modern TD DFT methods [13, 14] and soliton concept [15–19].

The similar collective systems of π-electrons are mobile and very sensitive to the various perturbations (injections of charge, deformation of σ-core, excitation by light quants) or/and to environment, including the solvent nature. The dependence electron structure deformation on the chemical constitution of the conjugated molecules could be investigated effectively by spectral methods so as the conjugated systems manifest the specific selective and highintensive bands both in the absorption and fluorescence spectra.

9.1.1 Classification

a. 1-Dimension Systems:

Linear conjugated systems (LCS) contain, as a rule, two terminal groups (TG) and polymethine chain (PC). In the general case, LCS with a non-branched PC can be represented as follows:

$$[G_1 - (CH)_m - G_2]^z, \qquad \mathbf{1}$$

where G_1 and G_2 are TG, m is the number of the methine groups, z is the charge ($z = 0; \pm 1$).

If $m = 2n + 1$, then neutral radicals ($z = 0$) are unstable; but the ionic systems ($z = \pm 1$) contrariwise system with closed electron shell are stable molecules with the oppositely charged counter ions; they are usually called as *polymethine dyes* (PDs). Of course, the stable cationic PDs contain the donor TGs; in the contrast, the stability of the anionic PDs is increased by introducing of acceptor end groups. The PDs with nitrogenous TGs trivially are called as *cyanine dyes* [20].

If number of methine component is even ($m = 2n$), such neutral molecules are treated as substituted *heteryl-polyenes* (HP) [1–4, 7]. The polyenes can contain both donor and acceptor TGs.

Symmetric PMD and HP differ substantially in several chemical and spectral properties. If linear conjugated systems have an asymmetric structure, the difference between PMD and HP decreases.

Besides, there exists another neutral 1-dimensional conjugated system containing simultaneously donor and acceptor terminal substituents **2**:

$$\text{Don} - (CH = CH)_n - \text{Ac}, \qquad \mathbf{2}$$

where Don is a donor TG while Ac is an acceptor TG; the n is denoted the number of the *vinylene* groups. Similar systems with extremely asymmetry are especially sensitive to the influence of various perturbations which could be registered by spectral measurements.

Here, we will regard two main types of the neutral donor-acceptor systems: merocyanines and cyanine bases, so as their spectral properties in the different solutions are studied in detail (see, for example, papers [21–24]).

Merocyanines. The first type of donor-acceptor compound can be presented by three resonance formulae **3–5**:

$$\underset{\mathbf{3}}{\text{Don} - (CH = CH)_n - CH = \text{Ac}} \leftrightarrow \underset{\mathbf{4}}{\text{Don}^+ = (CH - CH)_n = CH - \text{Ac}^-} \leftrightarrow$$

$$\leftrightarrow \underset{\mathbf{5.}}{\text{Don} - (CH \text{——} CH)^+_n - CH - \text{Ac}^-}$$

In contrast to non-charged response structure **3**, both other structures, **4** and **5**, are so-called “dipolar” contributing structures. In the first known merocyanines (in Brooker’s papers [25, 26], the symbol Don was an amino group and Ac was oxygen. Many other terminal groups Don and Ac with similar functionality can be used in merocyanines retaining the characteristics and hence may also be treated under the same name. In the structure **5**, the symbol A^- should formally treated as a donor group with high situated donor electronic level; there for merocyanines could be similar to the unsymmetrical polymethine dyes with two different terminal groups.

Cyanine bases: in contrast to merocyanines, the acceptor group in the cyanine dyes does not contain the high situated donor level, but low situated vacant level, and consequently they strongly differ on the related merocyanines. Neutral bases of cyanine dyes are obtained from cationic polymethines and hence are their de-alkylated derivatives. For example, case of the simplest cationic streptocyanine **6** produces its base **7**:

$$(H_3C)_2N^+{=}CH{-}\underset{\mathbf{6}}{(CH = CH)_n} - N(CH_3)_2 \Rightarrow H_3CN = CH - \underset{\mathbf{7}}{(CH = CH)_n} - N(CH_3)_2$$

Both merocyanines and bases as donor-acceptor compounds have high dipole moments that remain upon excitation and therefore they are effective sensors on the environment nature, especially, on the solution polarity.

b. Aggregates of PDs

It was observed, more than 70 years ago, an unusual behavior of some ionic cyanine dyes in aqueous solutions (see reviews [27, 28]). As regard to the solvent sensitivity, the absorption maximum was shifted bathochromically with increase of the concentration in water, and at high concentration the spectral bands became more intense and sharp. This tendency is typical for new absorption band: their sharpness with a small spectral wide and a very high absorption coefficient. Also, similar solutions demonstrate the strong fluorescence with small Stokes shift. This phenomenon of polymethine dyes in water solvents was explained by *aggregation*, and that the absorption spectrum was changed by the "vicinity effect" of adjacent molecules [28].

The dye aggregates that possess narrow absorption bands shifting bathochromically in comparison with monomer absorption band and nearly resonant fluorescence with small Stokes shift are generally termed Scheibe aggregates or J-aggregates, in the accordance with the name of their inventor (J denotes Jelley). Aggregates with hypsochromically shifted absorption bands are called H-aggregates (because of hypsochromic (H)) typically having low or absent fluorescence. Also, J-aggregates of other dyes, such as merocyanines, squaraines, etc. have been developed [27, 28]. Structural organization is important in considering of interaction between the dyes and carbon nanostructures, especially with fullerenes, antitumor agents [29–31]. The aggregation points in particular on the important influence of the solutions on the spectral properties of the linear conjugated systems.

9.1.2 Features of Electron Structure in Ground and Excited States

Electron Structure

According to Daehne' theoretical conception [1–4], in aromatic compounds, the C–C bond lengths are equalised while the carbon atoms have no noticeable charge, however the essential polarization of the C–H bonds causes to appearance of the appreciable positive charge at the carbon atoms and correspondingly charges with opposite sign at the hydrogen atom.

The polymethines and polyenes differ substantially on their electronic structure and hence on their chemical and physic properties. It is why, as a rule, they have been studied separately by the spectral methods [7, 8, 32, 33]. Particularly, the quantum-chemical calculation spectral data (^{13}CNMR) have shown that the considerable positive or negative charge alternates at neighboring carbon atoms in the extended chain of the polymethines in contrast to equalization of the bond lengths, that are approximately equal to 1.4 Å [4, 7, 8]. Going to the first excited state is accompanied by the little changes of the bond lengths, whereas the charges change significantly, even change their signs. In contrast, the atomic charges in the ground state in the polyenes are minimal (they appear by only C–H polarization), but the C–C bond lengths reach the maximum alternation, the amplitude of alternation in the long molecules reaching amounts to 0.08 Å. In the excited state, the bond lengths in the polyenes change significantly, so that following of the longer and shorter bonds is reversed (see, for example, the reviews [4, 7, 33] and the references therein).

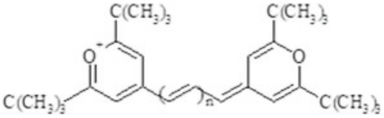
In is to be noted that similar classification of linear conjugated systems with an open electron shell (radicals) becomes more complicated. Thus, in the ionic polyene-radicals, the bond lengths and the electron density at the atoms are simultaneously equalized [34, 35]. Also, the simultaneous equalization of both electron density at the atoms and bond lengths is reached in the neutral polymethine because of the appearance of the unpaired electron [36]. Consequently, the π-electronic structure of the chain in both types of conjugated system is similar.

There is specific interest concerning thy on injection of the electrons or holes in the collective π-electron, as far as the π-molecules can be used as semiconductors. According to the modern conception, similar injection of the charge (positive or negative) in the highly polarized conjugate molecule causes appearance of the specific solitonic or impurity level in the energy gap, both the conductive and valence bands to bottom and top are shifted considerably [15–19, 37–39]. Then the injected charge could be treated as an ionic defect. It was shown that this charge or defect is not uniformly delocalized along the whole extended π-electron system, but is rather localized within several atoms. I.e. charge in the collective system forms the finite wave or the soliton (neutral for the radical and charged for cationic or anionic molecules). Performed quantum-chemical calculations have showed that the charge wave in the ions of the linear conjugated molecules is of a finite width covering 15–17 carbon atoms. Also, similar numeral calculations have given that the soliton becomes mobile, so that it can move from one terminal group to another group along the conjugated chain without a substantial change in the total energy of the molecule. It is to be noted that the similar movement of the solitonic wave is only possible when the length of the conjugated chain exceeds the dimension of the solitonic wave, what can accompanied by the symmetry breaking. It is logically, that the soliton-like wave of alternating bond lengths appears simultaneously with the charge alternation wave; it is treated as a geometrical soliton.

Thus, according to modern point view, the injected charge is neither localized in only one atom (π-center) nor uniformly delocalized along the conjugated system, but creates a solitonic wave of the alternating partial charges. Also, the quantum-chemical calculations have demonstrated that the multiple injections of the charges causes the generations of corresponding number of the solitons. It is important to notice that the location of the charge soliton depends on molecular topology and solvent polarity [8, 40].

Spectral Properties
The most specific feature of the conjugated systems is their comparatively narrow energy gap what enables the light absorption (and also fluorescence) in the different spectral regions (UV, visible and NIR). As regard to the linear systems, especially, PDs, the essential redistribution of the atomic charges and minimal changes in the lengths of bonds upon the light excitation provide the high intensive and narrow spectral bands (see, for example, reviews [5, 7, 8]).

Symmetrical cyanine dyes. The most intensive absorption is observed in the cationic PDs. As an impressive illustration, Fig. 9.2 presents the absorption spectra of the typical pyrylopolycycanines **8**:



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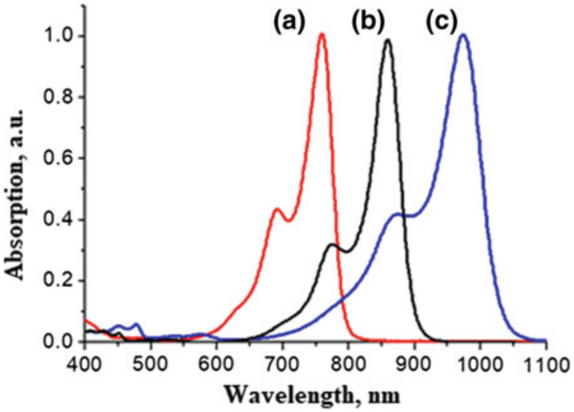


Fig. 9.2 Shift of maxima in the absorption spectra of dyes **8**; **a**: $n = 1$ (759 nm); **b**: $n = 2$ (860 nm), **c**: $n = 3$ (995 nm) (methanol) [8]

The PMD can undergo photoinduced geometrical isomerization in the excited state and hence to change essentially their absorption/fluorescence spectra what enable them to use widely as molecular switches [41–44], as well as fluorescence sensors, including biosensors [45–49]. PMDs have begun used in composites for solar cells, as far as they can convert light energy into electricity [50–52]. In this application, the dyes work as sensitizers, similarly to sensitization process in the photography.

Beside the ordinary electron transition from the ground state to the first excited state, $S_0 \rightarrow S_1$, there are the additionally possible high intensive transitions from the low excited states to the higher states, $S_n \rightarrow S_m$, as well as the effective two-photon absorption; these properties are perspective materials for the using of PMDs in non-linear optics [53–57].

Merocyanines. Since merocyanines as a D-A-conjugated compounds exhibit their intense absorption bands and the outstanding sensitivity of these bands to solvents, they attract high attention for different applications [55–58]. These features of the merocyanines are found to connect directly with their mobility of the electron density in collective conjugated system. It is supposed that merocyanines sensitivity of the absorption bands in the solvent could be simplest interpreted in terms of valence structures **3–5**, which assumes that the merocyanines the ground state (S_0) and excited state (S_1) are described by a linear combination of a non-charge-separated polyene-like structure **3** and charge-separated polyene-like structures **4**, **5**. In this model, increasing polarity of the solvent leads to increasing of the contribution of all charge-separated resonance structures, whereas the contribution of the neutral forms decreases. Experimental NMR spectroscopy confirms the redistribution of the atomic charges upon variation of solvent polarity [59]. When the balance of the contributions of the different valence structure is reached, this state is called as the “cyanine limit”.

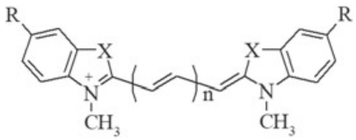
In is to be pointed that the transferring of the electron density along conjugation chain upon change of solvent polarity causes the essential change of the dipole moment direction and its value.

Cyanine bases. In another the donor-acceptor type, so-called cyanine bases, a donor and/or acceptor strength could be also varied regularly and purposefully to obtain the desired spectral characteristics. In these donor-acceptor molecules, the acceptor group is presented by nitrogen heterocycles that have more complex topology, the acceptor residues in merocyanines contain one-coordinated oxygen atom of the higher electronegativity [59]. Among the widest cyanine bases, styryl bases are most stable and hence are most studied (see review [60] and references therein). Going to the excited state is accompanied by the substantial intramolecular charge transfer, more often it is observed in the polar solvents.

As regard to spectral properties, bases exhibit, especially, in polar solvents, wide and structureless spectral bands, unlike the original cyanine dye with their narrow and high-intensive bands in the absorption and fluorescence spectra [24]; also bases show a considerable Stock’s shift. This fact can be explained by is intramolecular charge transfer (ICT) process upon excitation, whereas an electron density in PMDs transfers only on the adjacent atoms (see, for example, [60] and refers therein). Nevertheless, the cyanine bases as a specific donor-acceptor conjugated molecules are the finest fluorescent sensors; the cyanine bases in combination with a the crown complexing moiety, can be used as both the fluorescent quenchers so far the complexation with metal cations causes the drastic increasing of quantum yields, by a factor 100–1000 [59].

Both bases and chemically similar cationic cyanine dyes contain the same π-electron shell (the same number of π-electrons), however there the principal distinction between these two types of the donor-acceptor systems; it lies on the fact that the two-coordinated nitrogen atoms (for example, in the formulas **2**) have the electron configuration $\mathrm{N(tr^{2}trtr\pi)}$ while the electron configuration of the three-coordinated nitrogen is $\mathrm{N(trtrtr\pi^{2})}$. It is fact, which one must take into consideration of the electron-electron interaction upon describing the features of the electron structure of the neutral bases and interpretation of their spectral data; they determine the specific nature of the electron transitions in the bases in comparison with the initial cationic cyanine dyes. Going from cyanines to its base is accompanied by the essential equalization of the atomic charges and increasing of the alternation of the bond lengths in the extended chain. So, the amplitude of the charge alternation in the chain middle of the bases **7** is less, practically by factor 5–7, than in the initial cationic cyanines **6**. Besides, the distribution of the electron densities in the cyanine dyes is symmetrical, whereas, the some charge alternation in the chain of the cyanine bases changes regularly along the chain from one terminal group to another that. This transformation of charge distribution in the chain of the bases is high sensitive to the donor strength of the donor group, especially, close to this group.

The essential difference between cyanine dyes and their bases manifests itself most pronounced in absorption spectra. For sake illustration, the spectra of the some vinylogs of thiacyanines **9** and corresponding bases **10** are pictured in Fig. 9.3.



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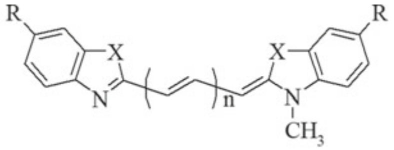


10

where X= S , R=H –**a**, $C(CH_3)_2$,R=H – **b**, $C(CH_3)_2$,R=NO_2 – **c**

Comparing spectra of cyanine dyes and related bases, one can see the considerable transformation of the longwavelength band. The cyanines **7** with different amount of vinilene groups from 0 to 2 possess high intensive and narrow spectral bands and the short wavelength shoulder corresponding to vibronical transitions, $0 \rightarrow 1'$ (Fig. 9.3a). The introducing of new vinylene, –CH=CH–groups in the chromophore (increasing of n) causes the bathochromic shift of the band maximum (so called vinylene shift) on 135 nm for $n = 0, 1$) and by 98 nm ($n = 1, 2$). Then the first vinylene shift (135 nm) is somewhat greater in compare with the usual value 100 nm; this can be explained

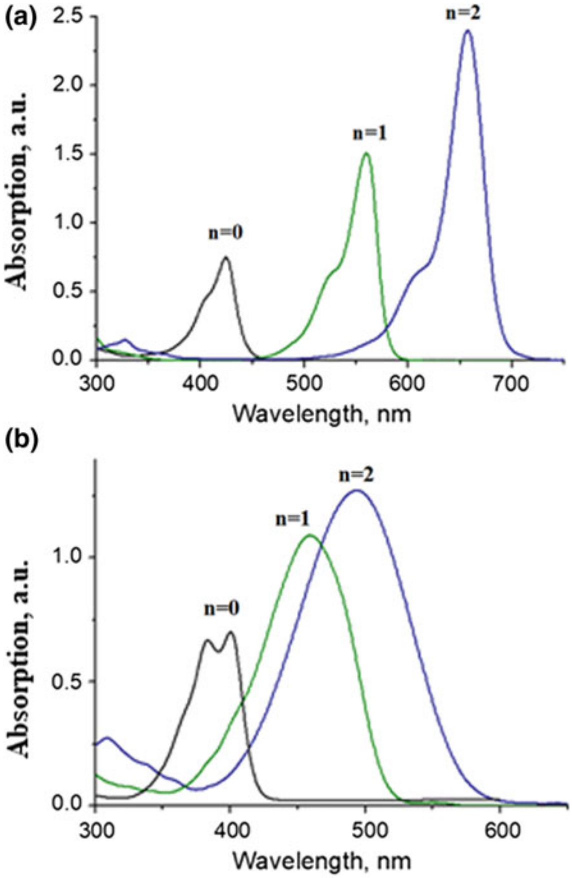


Fig. 9.3 Shift of the spectral maxima of the thiacyanines **9** (**a**) [81]; and base **10** (**b**), (concentrations $c = 1 \cdot 10^{-5}$ m/l, $c = 2 \cdot 10^{-5}$ m/l respectively, ethanol)

by an interaction between two sulfur atoms in the monomethinecyanine **7** ($n = 0$) which causes the hypsochromic shift of the band maximum [23, 24].

Figure 9.3b shows the transformation of the spectral bands of the bases in compare with spectra of the corresponding cyanine dyes; they are substantially wider and are hypsochromically shifted. Additionally, their vinylene shifts are lesser, 59 nm ($n =$ 0, 1) and 34 ($n = 1, 2$); and decreases upon lengthening of the chain.

The shapes of spectral band of the dyes **10(a–c)** are similar and differ only by the position of the maxima and widths, especially in polar solvents (see Table 9.1, too).

Comparing of spectral data in ethanol and acetonitrile and toluene shows that the absorption spectra of the considered cyanine bases are not highly sensitive to solvent polarity. One can also see from Fig. 9.3 that the going to higher vinilogs is accompanied by the regular increasing of the intensity of the spectral bands in the both cyanine dyes and bases.

Table 9.1 Position of the maxima of the band, λ_{max} (nm) and bandwidths $\Delta\nu$ (cm^{-1}) in bases **10** in solvents *acetonitrile (1)*, *toluene (2), ethanol (3)*

Dye	*1*		*2*		*3*	
	λ_{max}	$\Delta\nu$	λ_{max}	$\Delta\nu$	λ_{max}	$\Delta\nu$
10-a	452	3721	449	3670	459	3607
10-b	435	4130	435	4092	447	4036
10-c	500	4057	488	3827	505	4073

9.1.3 Influence of Solutions and Spectral Sensitivity

The unique mobility of the π-electron shell of the conjugated systems determines their high sensitivity to the environment medium, firstly, to solvent nature. This is basis for the convenient high sensitive spectral methods for study of such π-electron mobility: one- and two-photon absorption (OPA and TPA), both steady and time-resolved fluorescence, excited state absorption (ESA), etc. There are series of the papers concerning of influence of the polarity of solvents on the spectral properties [26, 32, 58, 61–67]. So, Table 9.2 presents the solvation effects for the pyrylo-4-cyanines and their heteroanalogues **11a** obtained in two various solvents (low-polar dichloromethane and higher polar nitromethane). Recently, it was established that the symmetric PDs demonstrate the low sensitivity to solvent polarity. Besides, it was experimentally found that absorption spectra of the ionic polymethine dyes with the enough long chain (absorbing on 1000 nm) undergo substantial transformation: the shape of the longwavelength band becomes unusually broad [67–73]. In is to be noticed that the long-wavelength side of the absorption band remains the same as in dyes with the shorter chain, in contrast to broad shoulder at the short-wavelength side. The analysis shows that this spectral effect is not caused by the growing of vibronical structure, as far as increasing of the solvent polarity leads this additional peak to be shifted regularly hypsochromically, as well as its intensity increases simultaneously. Figure 9.4 presents the absorption spectra of typical long cationic dye **12** in solvents of different polarity.

Table 9.2 Position of the maxima of the band, $\lambda_{max,}$ (nm) of pyrylocyanines and their heteroanalogues in solvents CH_2Cl_2 *(1)*, CH_3NO_2 *(2)*

n	11-a (X = O)		11-b (X = S)		11-c (X = Se)	
	1	*2*	*1*	*2*	*1*	*2*
0	555	552	630	627	673	672
1	686	676	762	755	805	795
2	806	798	889	879	930	922
3	–	–	1016	1000	–	–

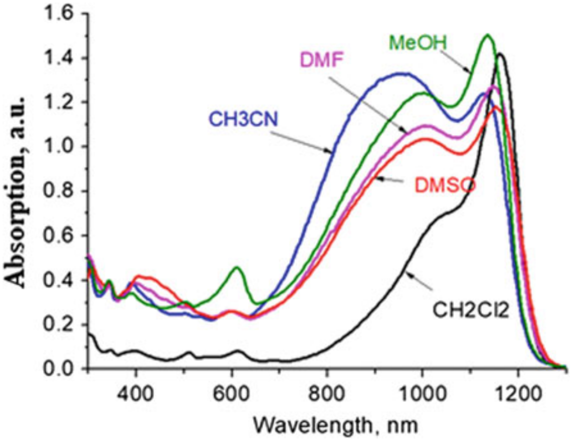
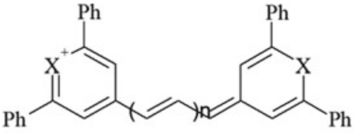


Fig. 9.4 Shape of spectral bands in various solvents [8]



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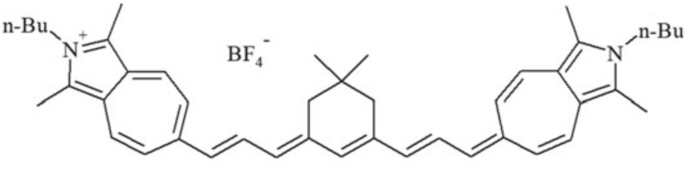
where X= O –**a;** X = S – **b;** X=Se – **c**



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The dyes with the comparative short chain exhibit typical absorption spectra; their absorption bands in both more polar and less polar solvents are enough narrow. But the width of the spectral bans of long dyes increases progressively upon increasing of the solvent polarity. Such widening is firstly connected with the appearance of additional broad shoulder on the short-wavelength side of the band. Then, this spectral fact points directly on the strong polarsolvatochromism. Figure 9.4 demonstrates that the long-wavelength band preserves its shape as in the shorter dyes. Consequently, it was assumed that two different forms of the dye with the long chain coexist in the solution: the first dye form with a comparatively low dipole oriented perpendicularly the chain (similarly to the short dyes) and the second dye form with a high dipole moment oriented along the chain. Similar mobility of the electron density distribution was studied quantum-chemically and can be explained in the framework of the soliton conception (see [8, 74] and numerous referrers therein). So, Painelli et al. [69] have shown the possible charge instability in polymethine dyes and their derivatives: they predicted the symmetry breaking in both the ground and the first excited state. Also, it was shown that quadrupolar chromophores can be classified as three types with different spectral properties. This theoretical model was illustrated by three representative quadrupolar chromophores: they exhibit the qualitatively different solvatochromic properties connected with the possibility of the symmetry breaking.

It should be pointed that the symmetry breaking can occur not only in ground state but also in the first excited state; this spectral effect was confirmed experimentally by time-dependent fluorescence upon the low-temperature [75, 76].

Basing on the spectral and quantum-chemical results, is was postulated that PDs with a polymethine chain containing crucial vinylene groups may exist in the ground state in two various charged forms, symmetrical and asymmetrical, correspondingly, with different distributions of the charge density [77]. Then appreciable difference between symmetrical and unsymmetrical forms of the dyes should display unambiguously the similar difference in their solvation effect, what agrees well with the measured spectral sensitivities of both forms to the solvent polarity.

Unsymmetrical Polymethine Dyes and Polyenes

Beside the symmetrical linear conjugated systems, the unsymmetrical compounds are also wide known; they are more sensitive to the solution nature [4, 5, 7, 32, 77, 78]. Traditionally, the unsymmetrical compounds are usually considered as derivatives of the corresponding symmetrical molecules which are usually referred to the *parent* compounds. In the construction of asymmetrical systems, a half of the molecule is taken from one symmetrical parent compound, the other half is taken from another parent compound.

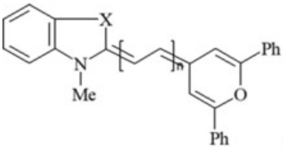
In unsymmetrical molecules, the collective π-electron shell shifts from the chain middle, which is obtained from quantum-chemical calculations [77]; it was established that the minimum of the calculated charge alternation amplitude in unsymmetrical dye is shifted to the benzene ring and reach the practically the bond length equalization, similarly to the polyenes. The same distortion of charge distribution is experimentally confirmed by spectra NMR (^{13}C) [77]; the chemical shifts for the neighboring carbon atoms are considerably alternated along the polymethine chain. So, the measurements have given that the signals close to both terminal ends in the unsymmetrical as well as in the parent symmetrical dyes are appreciable shifted in the weak field because of the influence of terminal groups [77]. It is logically that increasing of asymmetry degree by using of the more basic variable terminal group causes the increasing of bond length alternation degree and of decreasing of charge alternation in the polymethine chain.

The spectra of the unsymmetrical dyes turn out to be more sensitive to asymmetry; namely absorption spectra were used for the estimation of the asymmetry degree [32]. As convenient asymmetry parameter, the deviation D was proposed. By definition, this parameter is calculated by comparing of the spectra of the unsymmetrical dye and its both parent dyes:

$$\mathrm{D} = (\lambda_1 + \lambda_2)/2 - \lambda_{\mathrm{as}} \tag{9.1}$$

Here λ_{as} is the absorption maximum for unsymmetrical dye whereas λ_1 and λ_2 are maxima of both symmetrical parent molecules. The systematic measurements have shown that for typical unsymmetrical cyanines, $D > 0$, i.e. the maximum for unsymmetrical dyes is hypsochromically shifted in comparison with the arithmetic mean value from the maxima of the parent dyes. This spectral effect was explained by the generation of the appreciable bond alternation along the polymethine chain when the terminal groups in the dye are non-equivalent [32]. It was found that the bond alternation in the excited state decreases considerably; as a result, the deviation in the fluorescence spectra (when electron transition occur upon the excited state relaxed geometry) of the unsymmetrical PDs decreases essentially [78]. Of course, the deviations depend strongly on the solvent polarity.

The opposite spectral effects are observed in the unsymmetrical polyenes [78]. It was shown the violation of symmetry in polyenes leads to the opposite change in bond orders as compared to that in PMD: bonds in asymmetrical polyenes are more equalized than in the corresponding parent compounds. Then, the deviations calculated from formula (9.1) should be negative, which was proved by experimental studies of vinylogous series of asymmetrical polyenes **13** with one constant nucleus and variable residues. The spectral characteristics are listed in Table 9.3.



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Where X:CMe_2 –**a;** X: S – **b;**
X: CH=CH – **c**

As one can see, the deviations in unsymmetrical polyenes are really negative. Their absorption maximum is bathochromically shifted in the comparison with the arithmetic mean $(\lambda_1 + \lambda_2)/2$ of both symmetrical parent polyenes.

Donor-Acceptor Molecules

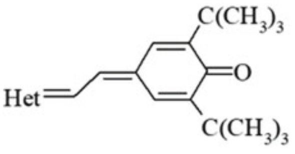
Among various unsymmetrical linear conjugated systems, the spectral of the neutral donor-acceptor molecules are most sensitive to solvent media. The considerable spectral effects are, of course, observed for the merocyanines (see, for example,

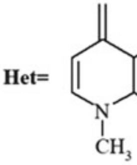
Table 9.3 Position of the maxima of the band, $\lambda_{max,}$ (nm) for heteroanalogues **13**. D is deviation; $V = \boldsymbol{\lambda}_{\mathbf{max}}(n) - \boldsymbol{\lambda}_{\mathbf{max}}(n-1)$ is vinylne shift

n	13-a (X:CMe_2)			11-b (X:S)			11-c (X:CH=CH)		
	λ_{max}	V (nm)	D	λ_{max}	V (nm)	D	λ_{max}	V (nm)	D
0	442	–	−18	454	–	−24.5	456.5	–	−80.5
1	472	30	−8.5	483.5	29	−10	495	38.5	−36.5
2	495	23	−7.5	506	29.5	−13	515.5	20.5	−32.5

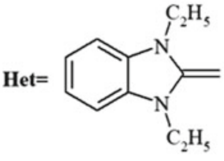
review [21] and refers therein) and related cyanine bases [24, 26, 79, 80]. Let us consider sequentially their spectra.

Merocyanines. As a worthwhile example, the absorption spectra of the merocyanines **14** derivatives of pyrole were examined; their spectra are pictured in [80].





14-a



14-b

14

One can see that not only the band maximum but also band hope depend on solvent polarity, when vibrational transitions clearly observed (Fig. 9.5). The lowest 0 → 0′ vibrational transition could exhibits in the spectra by various ways: by the intensive peak or by less intensive second peak or even by shoulder at the longwavelength side

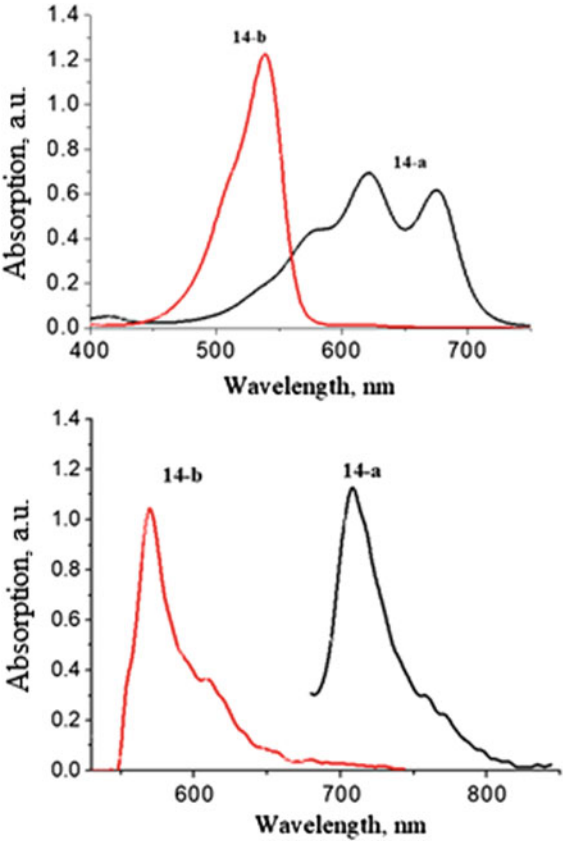


Fig. 9.5 Absorption (300 K) and fluorescence spectra (77 K) of the **14a–b** in acetonitrile ($\varepsilon \times 10^4, 1 \times \text{mole}^{-1} \times \text{cm}^{-1}$)

of the band. The observed change in the relative intensities of vibrational transitions can be attributed to the changes of bond lengths within the chromophore upon its relaxation from the excited state. In dyes with an slight change of equilibrium molecular geometry upon excitation, the most probable transition occurs from the ground state 0-th vibrational level to the excited state 0′-th vibrational level, and hence the intensity of $0 \rightarrow 0'$ transitions should be the highest.

The occupation of higher vibrational level is less probable, therefore the corresponding intensities of $0 \rightarrow 1'$ and $0 \rightarrow 2'$ transitions should be lower. The intensity ratio of the vibrational peaks could be inverted when the substantial change of bond lengths in the dye chain happens upon relaxation in the excited state. One can see that vibrational structure (transitions to higher vibrational states) sharply changed in the fluorescence spectra measured upon the low temperature, especially, for merocyanine **14-b** (Table 9.4).

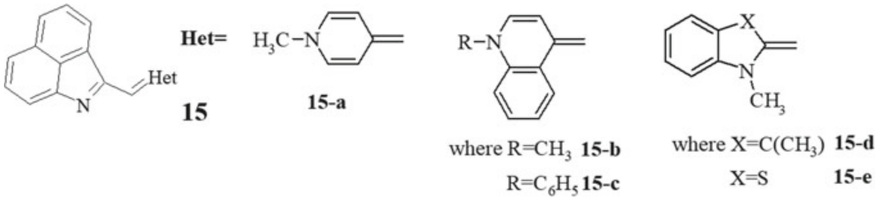
Donor-acceptor molecules; *cyaninebases*. In the absorption spectra of the cyanine bases, the separated bands connected with the first $\pi \rightarrow \pi^*$ electron transitions are also observed in the visible part. For sake illustration, the longwavelength bands of the dyes **15**a–e are pictured in Table 9.5.

Table 9.4 Spectral data of merocyanines **14**

	Absorbtion		Fluorescence			
	λ_{max} (nm)	$\varepsilon \times 10^4$ (l mole^{-1} cm^{-1})	λ_{max} (nm)	$\Delta\lambda$ (nm)	Stock's shift	
					$\Delta\lambda_S$ (nm)	$\Delta\nu_S$ (cm^{-1})
14-a	676	6.18	708	135	32	669
14-b	539	12.23	570	−3	31	1009

Table 9.5 Spectral data for cyanine base **15a–e**: a the absorption band maxima (λ_{max}, nm), extinction (ε, $\mathbf{10^4}$) in solvents 1—dioxane, 2—toluene, 3—acetonitrile, 4—methanol. $\boldsymbol{\lambda}^{\mathbf{theor}}$ (nm) is calculated wavelength of the first electron transition

	1		*2*		*3*		*4*		λ^{theor}
	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	
15a	1.58	569	1.85	567	5.57	571	9.70	523	522
15c	2.26	574	3.75	574	7.10	572	7.09	589	513
15b	3.57	582	3.21	583	7.01	584	6.76	569	531
15d	2.57	525	2.20	526	4.86	523	3.83	515	499
15e	2.20	519	2.08	520	4.06	515	2.88	508	472



One can see that all presented spectra have wide bands with the vibronic structure in both polar and non-polar solvents. Their vibronical transitions are revealed as the spectral band shoulders. In non-polar toluene, the vibronic structure is most pronounced. The measured distance between vibronic transitions reaches the 1100–1400 cm^{-1}, what is close to the corresponding value in the spectra of polymethine dyes and derivatives. One could see from Fig. 9.6 that 0 → 1′ vibronic transition in the absorption spectra of the investigated cyanine bases is the most intensive.

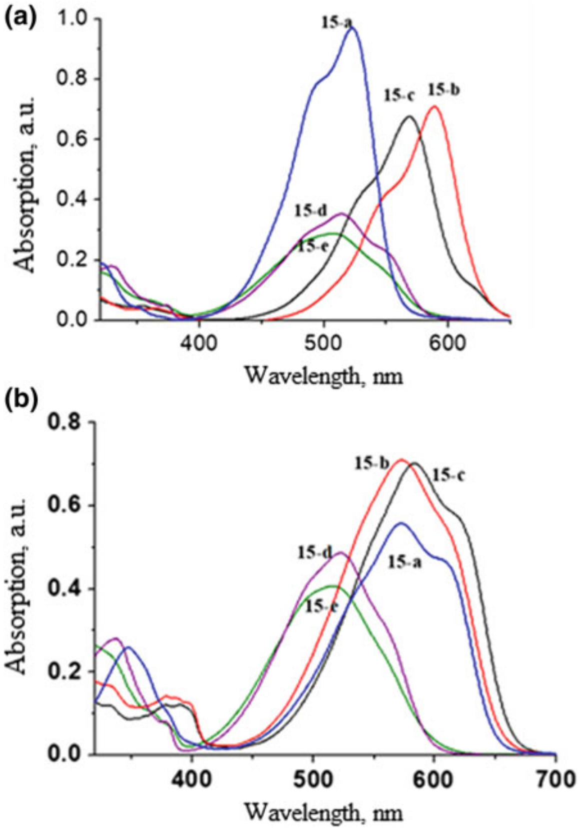


Fig. 9.6 Absorption spectra of bases **15a–e** at $c = 1{\times}10^{-5}$ M in different solvents: **a** methanol, **b** acetonitrile

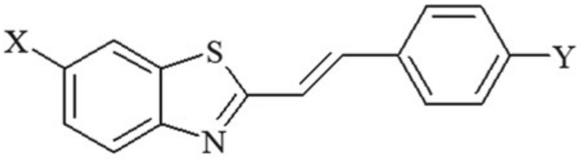
The longwavelength separated comparative intensive band in all solvents corresponds to only the first π → π*-electron transition, whereas the higher transitions is observed in the spectral region shorter than 400–450 nm. The positions of the maxima of the longwavelength bands of the dyes **15**a–e are collected in Table 9.5.

Both Fig. 9.6 and Table 9.5 data testify that spectral characteristics of the cyanine bases are not very sensitive to the solvent polarity One can see from Fig. 9.6b that the spectral bands in the polar acetonitrile are rather wide and structural, so that the fine vibronic structure is observed and 0 → 1′ vibronic transition is the most intensive.

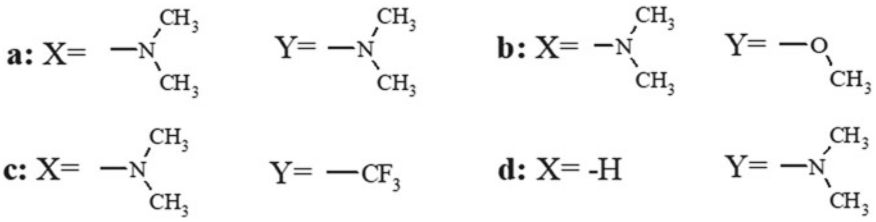
The careful study was shown that solutions of the cyanine bases **15a–e** are not stable. So, the intensity of absorption bands of the bases solutions upon exposure to air decreases regularly. Also, it was established that stability depends on the chemical constitution of the terminal donor group. The extinction coefficient decreases in serii: (in %) is: 15.71 (**15a**), 2.45 (**15b**), 5.45 (**15c**), 0.55 (**15d**) and 0.54 (**15e**).

Thus, Figs. 9.6 and 9.7 demonstrate appreciable influence of the polarity of the solvents on the spectral properties of the cyanine bases as the high sensitive neutral donor-acceptor compounds with the mobile collective system of the π-electrons.

At last, it has to be pointed that many cyanine bases can be weakly sensitive to the absorption spectra (i.e. electron transition upon the ground state equilibrium geometry), whereas are very sensitive to the fluorescence spectra, when electron transitions occur upon the excited state equilibrium geometry. As an illustration, the absorption and fluorescence spectra of cyanine bases **16** are pictured in Fig. 9.8. Also, spectral data collected in Table 9.6 testify about the high sensitivity of fluorescence maxima to the solvent polarity.



16



a: X= $-N(CH_3)_2$ Y= $-N(CH_3)_2$ **b:** X= $-N(CH_3)_2$ Y= $-OCH_3$

c: X= $-N(CH_3)_2$ Y= $-CF_3$ **d:** X= -H Y= $-N(CH_3)_2$

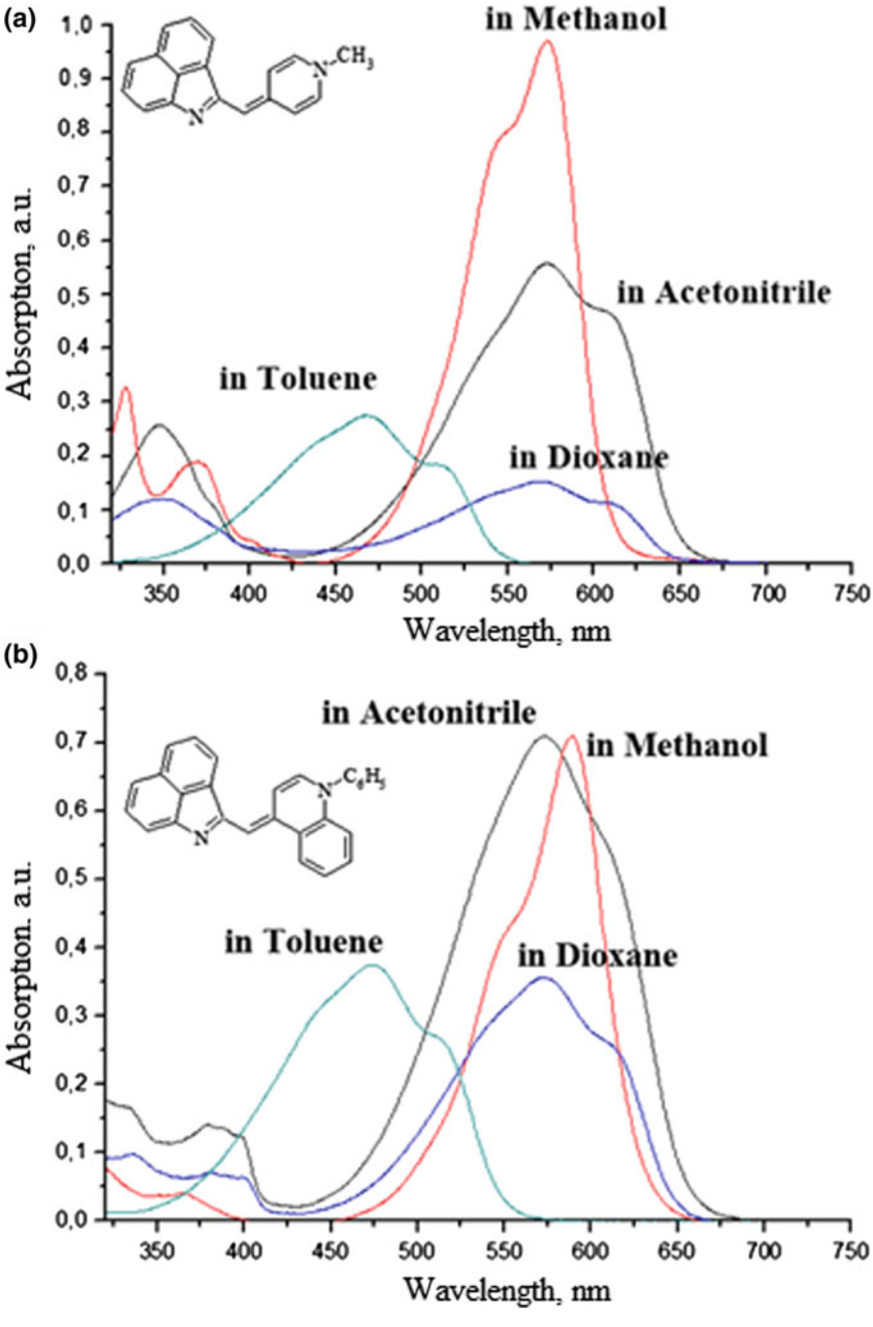


Fig. 9.7 Absorption spectra of bases, $c = 1 \times 10^{-5}$ M in different solvents: **a** 15a, **b** 15b

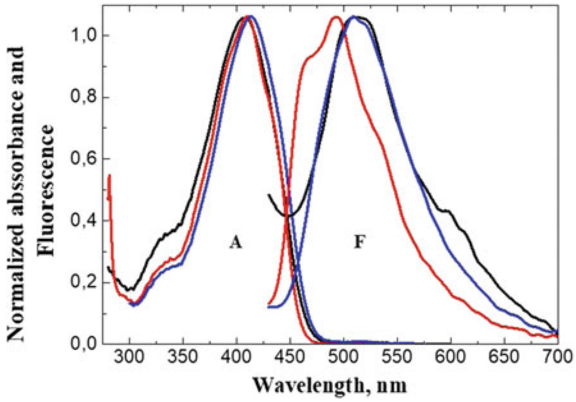


Fig. 9.8 Normalized absorbance (A) and fluorescence (F) spectra of **16a** (**a**) in toluene (red line), acetonitrile (black line) and methylene chloride (blue line)

Table 9.6 The main linear photophysical parameters of dyes **16 a–c**: absorption max λ_{ab} and fluorescence max λ_{fl} maxima, Stokes shifts (cm^{-1} (nm)), maximum extinction coefficients ε^{max} ($\times 10^{-3}$, M^{-1} cm^{-1}), calculated transition dipole moments $\mu_{\mathbf{01}}^{cal}$, D; fluorescence quantum yield Φ_{fl}, %; experimental τ_{fl}, ns (Ai)[a], (solvents with **c** with different polarity: 1—toluene, 2—DCM, 3—DMSO)

Solvent Comp.	1				2				3			
	16a	16b	16c	16d	16a	16b	16c	16d	16a	16b	16c	16d
λ_{ab}^{max} (nm)	410	393	410	395	414	394	410	400	419	399	416	408
λ_{fl}^{max} (nm)	491	480	499	491	506	496	531	497	515	525	590	522
Stokes shift	4020 (81)	4610 (87)	4350 (89)	4950 (96)	4390 (92)	5220 (102)	5560 (121)	4880 (97)	4450 (96)	6020 (126)	7090 (174)	5350 (114)
ε^{max}	35.9	26.8	26.9	25.2	27.0	29.5	26.0	32.3	33.7	26.8	24.5	26.1
$\mu_{\mathbf{01}}^{]textcal}$	7.9	6.8	7.2	6.4	7.1	7.6	7.4	7.4	8.6	7.4	7.2	6.8
Φ_{fl}	5	50	47	0.72	2.3	51	53	0.6	4	55	44	1.7
τ_{fl}	0.39	2.2	2.8	0.9	0.22	2.9	3.5	0.13	0.37	3.3	3.97	0.2

[a]Corresponding lifetime components

9.2 Conclusion

Thus, the high mobility of the collective π-electron shell in the linear conjugated molecules (and their ions) is confirmed by their spectral properties. This electron mobility depends on type of the conjugated system, chain length, symmetry, molecular constitution of the terminal groups, as well as the electron shell (neutral or charge system). Besides, different molecular types show the different sensitivity to the solvent polarity.

Acknowledgements Figures 9.2, 9.4 and 9.3, Table 9.1 are reprinted from: [8, 81]; Table 9.6 is reprinted from A.D. Kachkovsky, N.V. Pilipchuk, V.V. Kurdyukov, A.I. Tolmachev, Yu.L. Slominskii, V.Ya. Gayvoronsky, E.V. Shepelyavyy, S.V. Yakunin, M.S. Brodyn, Spectral and non-linear optical properties of cyanine bases' derivatives of benzo[c, d]indole, Dyes Pigments 74, 195–201 (2007) https://doi.org/10.1016/j.dyepig.2006.01.048, respectively with permission from Elsevier.

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