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Structure and spectral-luminescent properties of polymethine dyes

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ABSTRACT. The review considers the influence of the length of the polymethine chain, the structures of the hetero-radicals, the nature of substituents, electronic asymmetry, interactions of chromophores, structures of ion-pairs, photochemical reactions with proton transfer, and concentration, on the spectral-luminescent properties of polymethine dyes. The characteristic features of these properties in low-polarity media, including polymeric matrices, are discussed. Solvatochroism and solvatofluorochroism of polymethines are considered. Major factors influencing changes in the spectral-luminescent properties of cyanines, in relation to their structure and the nature of the medium, are revealed. Possible applications of polymethines to the solution of various problems connected with the transformation of light energy are discussed.

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I. Introduction

Polymethine (cyanine) dyes (PD) are unique agents for the transformation of light energy in the visible and near infrared region of the spectrum.[1] They are able to strengthen and to weaken radiation, to change its wave length and to sensitise and desensitise various photo-processes,[2–6] and are thus suitable for wide application in various areas of science and technology.[7] In order to search effectively for PD that are specifically able to transform light energy, it became necessary to establish a relationship between their chemical structure and spectral-luminescent properties.

In the course of the long history of investigations of PD, fundamental relationships were obtained linking coloration with structure, making possible the synthesis of dyes with desired absorption maxima λ^{a}_{max}.[8–10] In spite of such a long history of investigation, interest in PD has revived strongly in recent times. This has been caused primarily by the fact, that in addition to their traditional application in the photographic industry,[10,11] PD have found wide application from the mid-seventies in other fields of technology, especially in the rapidly growing area of quantum electronics.[2,5,12,13] Only by the application of PD as passive locks has it been possible to obtain laser impulses of extremely short duration: femtoseconds (using jet dye lasers) in the visible region (487–508,[14] 553–570,[15] 576–615,[16] 652–694 nm[17]) and picoseconds (using solid state lasers) in the near infrared region (750–790,[18] 1060,[19] 1320,[20] and 1540 nm[21]). New possibilities have thereby been opened up for the investigation of ultra-fast photo-processes in chemistry and biology.[22] At the present time, PD are the only organic dyes which can be used as active laser media to provide generation (i.e. to change the wave length of laser radiation) in the region >1000 nm: 1080–1170,[23] 1150–1240,[24] 1200–1320,[25] 1425,[26] 1550, 1600, and 1800 nm.[27] The passive synchronisation and generation of radiation in this region are of great interest in the fields of optical fibres and medicine.[28,29]

However, the specific search for cyanines for use in quantum electronics cannot be carried out effectively on the basis of a relationship linking only λ^{a}_{max} and structure of the PD.[8–10]. It became necessary to establish an analogous relationship for luminescence. But this was also soon found to be insufficient in the effective search for PD with the required properties, since identical values of λ^{a}_{max} and of λ^{f}_{max} may be associated with different dyes, which differ distinctly in such spectral-luminescent properties as quantum yield of fluorescence, φ, life time of the excited state, τ, and shape of the bands (especially their width, σ). These differences determine the assignment of the PD to the solution of one or another problem. Thus, dyes with small values of σ, φ, and τ are used as passive locks for quality modulation and mode synchronisation of optical quantum generators.[30,31] On the other hand, dyes with large values of these parameters are applied as active media for frequency conversion in lasers.[2,12] New spheres of application for PD have stimulated the investigation of their spectral-luminescent properties and have led to the appearance of numerous publications in the literature. However, there are no reviews of this work†.

In the present review, a systematic analysis of literature data, including work of the author in the field of spectral-luminescent properties of PD, is first carried out. Considerable attention is given to problems of directional change of the Stokes shift (ΔS) and quantum yields of fluorescence of PD, the characteristics of their spectral-luminescent properties in low polarity media (including

† Reviews are available on analogous topics for aromatic[32] and heterocyclic compounds.[33]

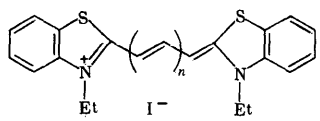
polymeric matrices), and the application of PD for the transformation of light energy. Prospects for future investigations of the spectral-luminescent properties of PD are considered.

II. Influence of the structure of the chromophore on the spectral-luminescent properties of polymethine dyes

Spectral-luminescent properties of polymethine dyes are due principally to their long-wave $\pi-\pi^*$ transition, the dipole moment of which is directed along the chain of conjugation from one heteroradical to the other. The probability of this transition is strongly dependent on structural changes in the chromophore. Therefore, the structure of the chromophore has an essential influence on the spectral-luminescent properties of PD.

1. Influence of the length of the polymethine chain on the spectral-luminescent properties of polymethine dyes

The polymethine chain (PC) is the major structural factor determining the spectral-luminescent properties of PD. In the example of the classical cyanine series of benzthiazoles, (I)–(V), it is seen that a change in chain length of only one vinylene group gives rise in symmetrical PD to a corresponding change in both λ^a_{max} [34] and λ^f_{max} [35] of about 100 nm. This agrees well with theoretical predictions of the change in position of electronic bands, with the length of the PC.[36,37]



(I) - (V)

Dye	n	λ^a_{max}, nm	λ^a_{max}, nm (CH_2Cl_2)
(I)	1	560	580
(II)	2	665	683
(III)	3	770	793
(IV)	4	895	918
(V)	5	1000	1023

The shapes of the bands in the absorption and fluorescence spectra, in contrast to their maxima, change in different ways with increase of n (Fig. 1*a*, *b*). Lengthening of the PC leads to a sharp fall in the selectivity of absorption (to a decrease in intensity and widening of the bands).[34] In addition, the dependence of the shape of the absorption bands on the nature of the solvent is increased (Fig. 1*a*). Conversely, the fluorescence bands become narrower with increase of n, and their shape is practically independent of the nature of the solvent[38] (Fig. 1*b*).

The shapes of the absorption and fluorescence bands of PD are determined mainly by vibrational and intermolecular interactions.[34,39] With increase of n in symmetrical cyanines, the former gradually become less, but the latter increase in strength.[34] A decrease in vibrational interactions leads to a narrowing of the bands, and an increase in intermolecular interaction leads, conversely, to broadening.[34] In the spectra of the thiocyanines (I)–(V), the described effects are explained by the dominant role of intermolecular interactions in absorption and of vibrational interactions in fluorescence.[38]

The length of the PC has a considerable effect on the quantum yield of fluorescence. Thus, for the symmetrical thiocyanines (I)–(V) and their analogues with benzoxazole and indolene radicals, the magnitude of φ increases with increase of n from 0 to 2–3.[35] For $n > 3$ the quantum yield for these PD decreases sharply.[35] For $n = 0$ and $n \geqslant 4$, the magnitude of φ is $< 1\%$. In the case of di- and tri-carbocyanines, φ varies within the range 25–58%.[35]

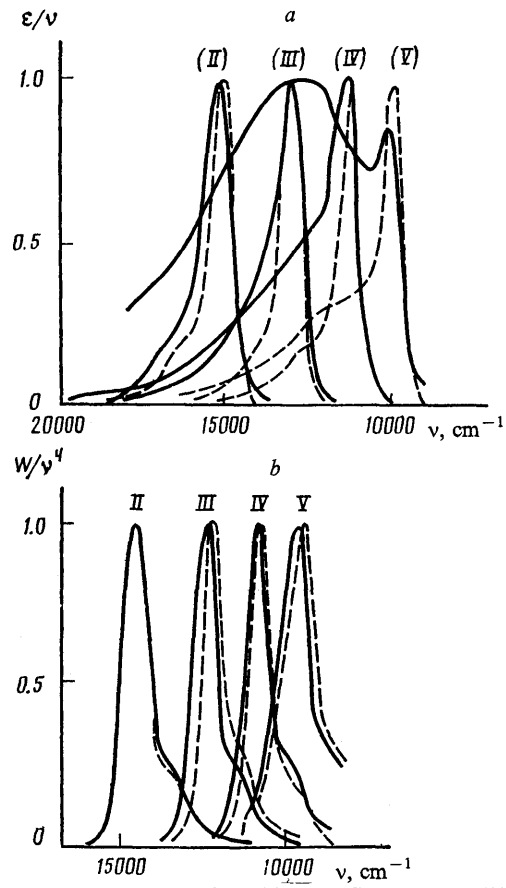
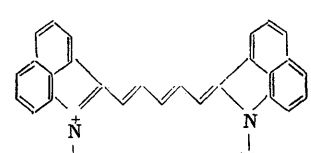
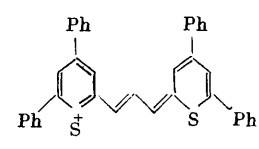


Figure 1. Absorption (*a*) and fluorescence (*b*) spectra for PD (II)–(V) in CH_2Cl_2 (dotted lines) and in DMF (continuous lines).

Small values of φ for the lower vinylogues are caused by effects arising from the close proximity of the nuclei, leading either to deviation from coplanarity,[40] or to interaction between the non-bonded heteroatoms.[41] The fall in the quantum yield of fluorescence with the higher vinylogues is caused, apparently, by the increased probability of internal conversion with increase of n, on account of a decrease in the energy difference between the ground (S_0) and first excited (S_1) states.[43,44] Such an assertion accords well with the fact that cyanines (VI) (λ^a_{max} = 876 nm, φ = 0.1%) and (VII) (λ^a_{max} = 865 nm, φ = 0.2%), with much shorter PC than the tetracarbocyanine (IV) whilst absorbing in practically the same region,[35] have almost the same values of φ.



(VI)



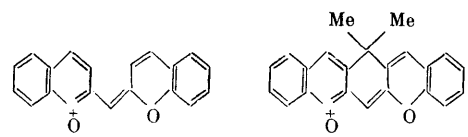
(VII)

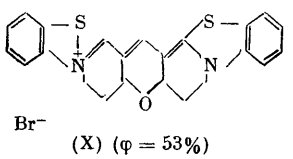
The life times of the excited states of PD vary with increase in n in the same way as the quantum yields of fluorescence, since the change in τ[45–47] with lengthening of the PC results from the same causes as the change in φ.

Attention is drawn to the fact that for PD with an open PC, even in the optimum region of absorption in which internal conversion is a minimum, the quantum yields of fluorescence are mainly in the region of 20–40% and only in the case of oxatricarbocyanine, φ = 58%.[35] Moreover, it is possible that the latter value is overestimated, as are the values of φ for thio- and indotricarbocyanines, since later measurements on these PD by other authors[48] gave smaller magnitudes for φ on the second occasion. These facts indicate that low values of quantum yields for PD with open PC are linked not only with internal conversion but also with the nature of the chain.

In symmetrical PD, the lengths of the carbon–carbon bonds are to a large extent equalised, as in aromatic compounds, and approximate to a bond order of one and a half.[49] Therefore rotation about these bonds is difficult by comparison with ordinary bonds. Nevertheless, the energy required is not large (33–63 kJ mol^{-1}).[40] In the ground state, dyes having no substituents in the PC and with $n \geqslant 1$ exist mainly as all-*trans* isomers.[4,40] With the introduction of bulky substituents into the PC, rotation about the bonds occurs, leading to the formation of various types of *cis*-isomer.[4,40]

With electronic excitation, the order of the carbon–carbon bonds decreases considerably,[50] so that rotation becomes easier. Therefore PD easily form photoisomers, which serve as basic "channels" for deactivation of the electronic excitation energy of cyanines.[4] The formation of photoisomers causes a sharp reduction in both the quantum yield and the life-time of the excited state.[3,51–53] Therefore, in spite of the fact that the oxygen analogue of PD (II), widely known as DODCI, possesses a nanosecond τ in its normal state, it is effective for passive mode synchronisation in dye lasers under pico- and even femto-second conditions[54] (it works as a short-life photoisomer[55,56]). It should be noted, that deactivation of the excited state will occur not only through rotations about the carbon–carbon bonds of the PC, but also through torsional vibrations about them.[3,4] If these rotations or vibrations are not hindered, then no structural changes whatever, which favour an increase in φ, wil be able to raise it to a value approaching 100%.



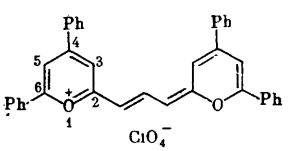


One way to solve this problem is by fixing the links of the PC rigidly with the aid of saturated bridging groups. Thus, for the monomethine cyanine (VIII), with an open PC, fluorescence is not visibly observed because of the low value of φ.[57] In the case of its analogue (IX), which has a rigidly fixed chromophore, such a strong golden-yellow luminescence is "kindled", that it masks the true crimsom colour of the dye which is like that of the compound (VIII). A sharp increase in φ is also observed by fixing the links of the PC of trimethine cyanines as, for example, in the case of PD (X).[58–60] In its benzoxazole analogues, φ = 80–90%.[58–60] Cyanines with completely fixed PC, containing five or more methine groups, are not known at present. There are certain PD with long PC, in which some of the groups form part of a saturated cyclic grouping,[61] but the fixing of separate parts of the PC only does not have such a significant effect on the value of φ,[62–65] as in the cases considered above.[58–60]

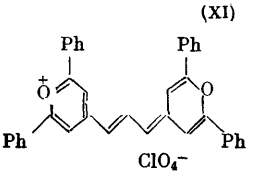
2. Influence of the structures of hetero-radicals on the spectro-luminescent properties of polymethine dyes

The structures of the hetero-radicals exert a very strong influence on the spectral-luminescent properties of PD. Thus, replacement of the benzthiazole nucleus in the dyes (I) and (II) with thiopyran or benz[*c*,*d*]indole groups [PD (VI) and (VII) respectively] gives rise to practically the same change in the absorption and fluorescence bands as does lengthening of the PC by two (*ca.* 200 nm) and three (*ca.* 300 nm) vinylene groups. In this way it is possible to obtain deeply coloured luminophores with short PC. Interest in such PD depends firstly on the fact that they are much more stable than dyes with long PC.[8,9]

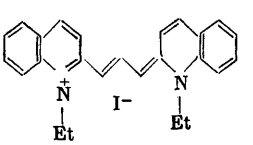
Isomeric change in the hetero-radicals has a significant effect on the spectral-luminescent properties of PD. Thus, cyanines in which the pyranyl or thiopyranyl heterocycles are linked to the chromophore by atom C(2) [PD (XI)], absorb or luminesce in a significantly longer wavelength region of the spectrum than their isomers, the pyran-4-yl (or thiopyran-4-yl) cyanines [PD (XII)].[41] For the nitrogen analogues of PD (XI) and (XII)[41] and the quinocyanine PD (XIII) and (XIV)[66] the opposite is true.



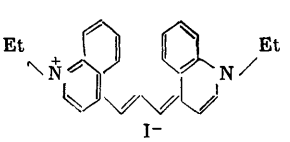
(XI)



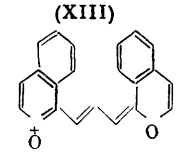
(XII)



(XIII)



(XIV)



(XV)

PD	λ^{a}_{max}, nm (CH_2Cl_2)	σ, cm^{-1}	φ, %	τ, ps	δ
(XI)	800	1176	1	—	0.176
(XII)	686	801	9	—	0.116
(XIII)	607	975	$\leqslant$ 0.01	9	0.182
(XIV)	713	769	2	37	0.083
(XV)	706	964	5	—	0.142

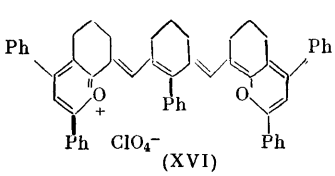
This is due to the fact that in pyran-2-yl- and thiopyran-2-yl-cyanines the carbon–carbon bonds in the hetero-radicals participate less in the general system of conjugation than in the pyrid-2-ylcyanines because of the smaller tendency to conjugation of atoms of oxygen and sulphur in comparison with atoms of nitrogen.[41]

Isomerism of the hetero-radicals is also strongly reflected in the shapes of the electronic bands of PD. The majority of symmetrical cyanines, including (XII) and (XIV) have characteristic spectral curves of similar shape, with vibrational maxima in their short-wave region.[67,68] For pyran-2-ylcyanines and their analogues there are anomalies. At room temperature the spectral curves of these compounds [for example, for (IX), (XI), and (XIII)] have four vibrational maxima[57,69,70] which is not uncommon for complex organic dyes.[71,72] For the 2-isomers, the absorption and luminescence bands are quite broad,[41,66,73–75] but the magnitudes of φ and of τ[76,77] are substantially less than for PD of types (XII) and (XIV).

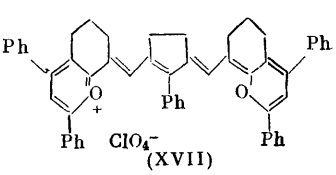
On the basis of quantum mechanical calculations using the squares of the changes in bond order (δ) on excitation[78] as a quantitative measure of the vibrational interactions in the PD chromophores, it was shown that there is an intensification of the vibrational structure, and a consequent widening of the bands, on going from the 4- to the 2-isomer in the pyranylcyanine series and their analogues.[79] Such an intensification is caused primarily by a sharp reduction in bond order between atoms C(3) and C(4) on excitation, a change which considerably exceeds that for all other bonds and which accounts for a significant contribution to the total magnitude of δ.[79]

Hence it follows that any structural modifications of the hetero-radicals of pyran-2-ylcyanines and their analogues, which hinder a change in the length of the bond between atoms C(3) and C(4), must lead to a weakening of the vibrational interactions. This can be achieved quite effectively as a result of annelation involving this bond, since a lowering of its order in the ground state decreases the extent to which it can change on excitation. Indeed, the bond between atoms C(3) and C(4) in cyanine (XV) contributes only 4% to the total magnitude of δ, whereas the analogous bond in the dye (XI) contributes 33%.[79] As a result, for PD (XV), a weakening of the vibrational interactions occurs, accompanied by a narrowing of the absorption bands in comparison to the analogous bands for compound (XI).

Vibrational interactions in molecules of PD are among the fundamental factors giving rise to a reduction in φ and τ.[80,81] It is very likely, therefore, that attenuation of their magnitude on going from the 4- to the 2-isomers is caused by an intensification of vibrational interactions. This assertion accords with the fact, that the excited states for pyran-2-yltricarbocyanines (XVI) and (XVII) have unusually short life times ($\leqslant 3$ ps).[19,77] Such small values of τ have made it possible to use PD (XVI) and (XVII) and their analogues as passive locks for lasers, with λ = 1060 nm, in order to generate impulses of extremely short duration.[19,77,82,83]



(XVI)



(XVII)

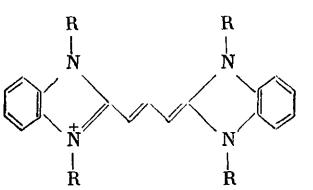
It should be noted, however, that the pyran-2-yl- and thiopyran-2-yl-cyanines are much more deeply coloured than the 4-isomers (by *ca.* 100–110 nm).[41] It can therefore be assumed that the reduction in φ and τ, on going from the latter to the former, is caused[43,44] by an increase in internal conversions. However, for the isomeric quinocyanines (XIII) and (XIV), the same tendency is observed in the changes in φ and in τ, in spite of the fact that pinacyanol (XIII) absorbs in a considerably more short-wave region (at 106 nm), than cryptocyanine (XIV). It can therefore be assumed that vibrational interactions play a dominant role in the reduction of φ and τ, on going from the 2- to the 4-isomer.

3. Influence of the nature of the substituents on the spectral-luminescent properties of polymethine dyes

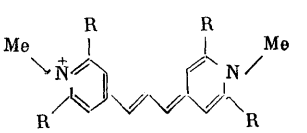
To regulate the extent of vibrational interactions in molecules of PD it is possible to introduce substituents with various electronic characteristics[84] into different positions of the heteroradicals[85–90] and into the PC.[91,92] For example, additional intensification of the vibrational interactions and a consequent shortening of the life time of the excited state of the pyran-2-yltricarbocyanines (XVI) and (XVII) is achieved on account of the electron-donating saturated cyclic groupings.[92]

Substituents containing heavy atoms, for example bromine and iodine,[4] have a considerable influence on the deactivation of electronically-excited states. They significantly increase the probability of intersystem crossing $S_1 \rightsquigarrow T$, because of the sharply decreasing values of φ and τ corresponding to the PD.[93] The role of such substituents in PC is more important than in the hetero-radicals.[93]

Substituents with their own conjugated electron system, such as those that are able to increase the Stokes shift of the PD molecules significantly, are of great interest.[93] Thus, the replacement of ethyl groups in the cyanine (XVIII) by phenyl [PD (XIX)], or better still by a heterocycle [PD (XX)], leads to an increase in ΔS and in φ.[94]



(XVIII)—(XX)



(XXI), (XXII)

PD	R	λ^a_{max}, nm	λ^f_{max}, nm	φ, % (ethanol)
(XVIII)	Et	500	515	0.5
(XIX)	Ph	519	563	5
(XX)	Py	530	593	25

PD	R	λ^a_{max}, nm	λ^f_{max}, nm (CH_2Cl_2)
(XXI)	Me	610	620
(XXII)	Ph	644	673

These effects have been shown to be associated with intramolecular processes. The increase in φ, by the introduction of substituents with their own π-system, is thought to be due to a decrease in the probability of the formation of stereoisomers, on account of "weighting" of the PD molecule with these substituents.[94] The increase of the Stokes shifts in the cited work is not explained. However, an explanation may easily be given on the basis of an analysis of the change in electronic structure of PD (XIX) and (XX) on excitation.

In the ground state of cyanine molecules (XIX) and (XX), the phenyl and pyridyl groups are displaced from the plane of the basic chromophore to a considerable extent, on account of steric hindrance by the atoms of hydrogen in positions 4,4′; 7,7′; and

8,8′. In the excited state, it follows from simple Hückel molecular orbital calculations for PD (XIX) (Fig. 2), that the bonds between N and C(2); C(4) and C(3*a*); C(7) and C(7*a*) are lengthened significantly. (In the calculations the parameters used were taken from Ref. 95, the angle of rotation of the phenyl group being represented by a value of $\beta_{C-Ph} = 0.7$). The steric hindrance to rotation of the phenyl groups is thereby reduced and they can therefore become much more nearly coplanar on excitation. Approach to coplanarity will also be favoured by the fact that in the excited state the N–Ph bond order is increased. A more planar structure for the phenyl (or pyridyl) substituted PD, (XIX) and (XX), in the excited state, compared with the ground state, leads to a larger bathochromic shift of the fluorescence bands than for the absorption bands. Therefore, a change from cyanine (XVIII) to (XIX) or (XX), is accompanied by an increase in ΔS.

On the basis of the above, it can be concluded that the introduction into a PD molecule of substituents with their own conjugated electron systems, capable of becoming more nearly coplanar on excitation, brings about an increase in the Stokes shift. Indeed, the replacement of methyl groups in the cyanine (XXI) by phenyl [PD (XXII)], increases ΔS. This arises from the fact that steric hindrance between the Ph and methyl groups in the ground state gives rise to a considerable departure from coplanarity with the chromophore,[96] but in the excited state, as a result of a decrease in the bond order of the bonds between the atoms of C and N and an increase in the order of the Ph–C bonds (Fig. 2), the groups becomes much more nearly coplanar.

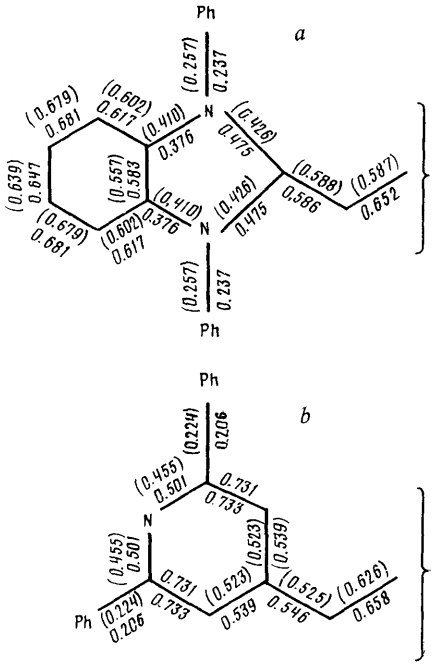
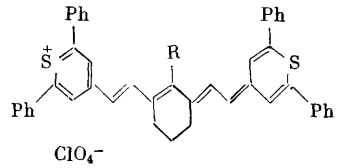


Figure 2. Orders of the π-bonds in the cations of PD (XIX) (*a*) and (XXII) (*b*) in the ground state and (in brackets) the excited state.

An analogous change in the conformation of the phenyl groups on excitation explains the anomalous Stokes shifts for 2,6-diphenyl substituted pyridine salts.[97–100]

In the *meso*-position of tricarbocyanines, the phenyl group also deviates considerably from the plane of the chromophore in the ground state.[101] However, replacement of the hydrogen atom in this position in the thiopyran-4-yltricarbocyanine (XXIII) with a phenyl group (compound XXIV) does not in practice increase ΔS.[102] The phenyl group in PD (XXIV) moves little towards coplanarity in the excited state.

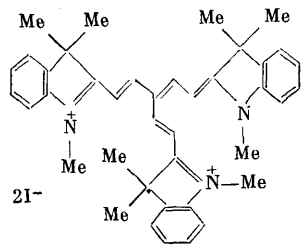


(XXIII), (XXIV)

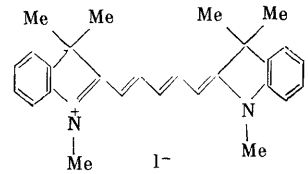
PD	R	λ^a_{max}, nm	λ^f_{max}, nm (CH_2Cl_2)
(XXIII)	H	1035	1090
(XXIV)	Ph	1040	1097

Especially large increases in Stokes shifts occur with the introduction into the *meso*-position of substituents that lead to branching of the PC, i.e. to the formation of tricyclic PD, for example (XXV), and its analogues.[103,104]

The magnitude of ΔS for the tricyclic dye (XXV) (1597 cm^{-1}) is almost twice that for the corresponding bicyclic PD (XXVI) (632 cm^{-1}).



(XXV): $\lambda^a_{max} = 636$ nm, $\lambda^f_{max} = 698$ nm



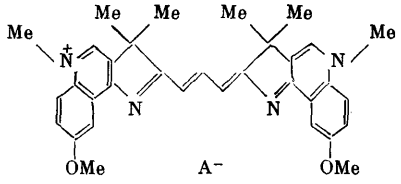
(XXVI): $\lambda^a_{max} = 640$ nm, $\lambda^f_{max} = 667$ nm.

Such a marked effect depends on the considerable change in geometry that occurs on excitation of the molecule (XXV) compared to (XXVI). In the ground state, tricyclic dyes have a propellor-like structure but in the excited state each of their nuclei in turn becomes perpendicular to the plane of the other two.[103,104] In bicyclic cyanines, excitation mainly brings about a change in bond lengths.

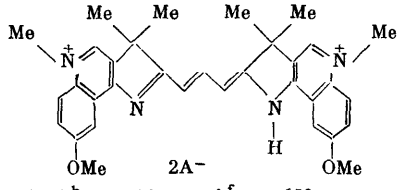
An increase in the Stokes shifts for PD (XXV) and its analogues is accompanied, in contrast to cyanines (XVIII)–(XX), by a marked lowering of φ.[104,105] This is linked with the fact that for tricyclic dyes the coplanarity is disturbed and there is a much more pronounced alternation of the bonds in the PC, than in the corresponding bicyclic dyes.[103,104] Consequently, the vibrational interactions and conformational processes are intensified in the former by comparison with the latter, with the result that PD (XXV) fluoresces much more weakly than (XXVI).

4. Photochemical reactions with proton transfer

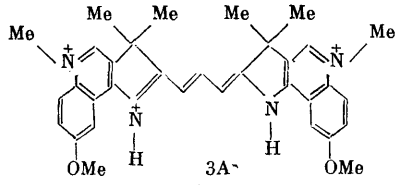
Large values of Stokes shifts and high quantum yields of fluorescence can be achieved for certain PD, for example (XXVII), through reversible photochemical reactions with proton transfer.[106,107] In absolute ethanol, this dye exists in the monocationic form (XXVII, a). On acidification with weak acids the protonated, dicationic form (XXVII, b), is produced. As a result, the electronic symmetry is disturbed and the conjugation of the chain is shortened, so that it absorbs in a considerably more short-wave region of the spectrum, than (XXVII, a). In strongly acidic solutions, compound (XXVII)



(XXVII, a): $\lambda^a_{max}=710$ nm; $\lambda^f_{max}=735$ nm; $\varphi=24\%$,



(XXVII, b): $\lambda^b_{max}=530$ nm; $\lambda^f_{max}=650$ nm; $\varphi=7\%$,



(XXVII, c): $\lambda^a_{max}=600$ nm; $\lambda^f_{max}=620$ nm; $\varphi=3.5\%$,

exists in the diprotonated, tricationic form, (XXVII, c). In this case the electronic symmetry of the molecule is restored, but the chain of conjugation becomes shorter. The absorption band of form (XVII, c) is therefore found in an intermediate region between the forms (XXVII, a) and (XXVII, b). For the PD (XVII) in the ground state there is an equilibrium (XXVII, a)$\rightleftharpoons$(XVII, b) or (XVII, b)$\rightleftharpoons$(XXVII, c), depending on the pH.

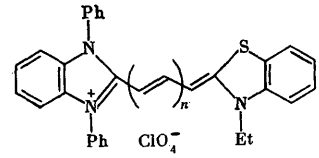
On excitation form (XXVII, b) results, with the loss of a proton, on account of redistribution of electron density in the chromophore. Therefore in the fluorescence spectra, in addition to the band of the dication (XXVII, c) the band responsible for the form (XXVII, a) appears, with a high value of φ, providing a large Stoke shift relative to the absorption of form (XXVII, b). This has made it possibe to use the equilibrium (XXVII, b)$\rightleftharpoons$(XXVII, a) for the generation of laser emission in the region of 720–810 nm, i.e. with a large shift relative to the wave length pumped, λ_P (λ_P = 530 nm).[106,107]

The form (XXVII, c) does not generate emission, most probably because of the low value of φ. In addition, it does not change on excitation into form (XXVII, b), or into form (XXVII, a). The first transformation does not occur because dissociation of the diprotonated form with formation of the excited monoprotonated form is energetically unfavourable, and the second is of low probability since it requires the simultaneous transfer of two protons.

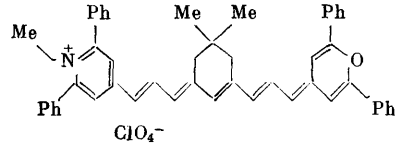
Photochemical reactions with proton transfer are highly sensitive to change in pH of the medium and are only characteristic of a small number of PD. These circumstances give rise to their wide application for the transformation of light energy.

5. Electronic asymmetry and spectral-luminescent properties of polymethine dyes

Asymmetrical PD are far more promising for the transformation of light energy.



(XXVIII) – (XXX)



(XXXI)

PD	n	Solvent	λ^a_{max}, nm	D^a_λ, nm	λ^f_{max}, nm	D^f_λ, nm
(XXVIII)	1	DMF	528	13	567	7.5
(XXIX)	2	DMF	618	22	670	2.5
(XXX)	3	DMF	645	95	779	5.0
(XXXI)	—	MeCN	610	387.5	1020	35.0

In the ground state of these cations the charge is mainly localised on the more electron-donating nucleus,[108–111] so that an alternation of single and double bonds arises in the PC leading, in the absorption spectra, to a rise in the deviation (D^a_λ), attenuation of the vinylenic shifts, and broadening of the bands.[108–111]

In the excited state, the nuclei of the hetero-radicals become equivalent to a considerable extent. For example, in the S_1-state of PD (XXX),[111] the total charges on the benzimidazole and benzthiazole radicals amount to 0.640 and 0.631, whereas in the S_0 state they are 0.858 and 0.388 respectively. Equalisation of the charges on the hetero-radicals and, consequently, equalisation of their electron-donating abilities, greatly reduces the alternation in the bond order in the PC of the cation in the excited state. Thus, for example, a measure of their alternation, calculated as described[57] for the dye (XXX) in the excited state, is 0.098 but in the ground state is 0.126. Consequently, typical electronically-asymmetric PD tend towards electronic symmetry in the excited state. This leads to a sharp decrease in the deviation in the fluorescence spectra (D^f_λ), a narrowing of their bands, and a rise in the vinylenic shifts of approximately 100 nm, i.e. to values characteristic of symmetrical PD. Asymmetric PD also retain high values of φ, at the level of the symmetrical PD.[112]

A marked difference in the electronic structure of asymmetric PD in the ground and excited states causes a large Stokes shift. Since this occurs for high values of φ, then highly effective generation of radiation was obtained for solutions of asymmetric cyanines in the near infrared region (650–900 nm).[112,113] It is significant, that in view of their wide absorption bands,[111-113] the generation of emission by PD of types (XXVIII)–(XXX) occurs with a pump of different

wave length from the most used sources of radiation in the visible range (510, 530, 578, 694 nm).[112,113] Asymmetric PD are advantageously different in this respect from the wide range of active media based on coumarins, rhodamines and oxazines.[112,114]

Variations between the absorption and fluorescence spectra of asymmetrical PD are more significant, the greater their electronic asymmetry. The latter increases regularly with increase in the difference in electron donating ability of the hetero-radicals and with the length of the PC.[109–111]

Pyrid-4-yl-pyran-4-yl-tetra- and -pentacarbocyanines have been described,[115] with the highest electronic asymmetry amongst organic dyes. In their absorption spectra, the deviation amounts to 545 nm (7450 cm^{-1}). However, these PD approach the symmetrical cyanines to a considerable extent in their luminescent properties in the excited state.[115] In the fluorescence spectra, the deviation falls to 35–65 nm (320–650 cm^{-1}).[115] The Stokes shift for PD (XXXI) amounts to 410 nm (6590 cm^{-1}), the highest value for all known dyes (Fig. 3). Unfortunately, the quantum yield of fluorescence is extremely small (< 0.01%) because, apparently, of strong vibrational interactions.[115]

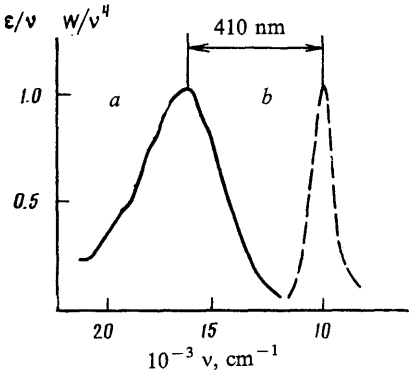
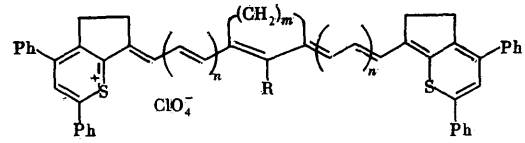


Figure 3. Absorption (*a*) and fluorescence (*b*) spectra of PD (XXXI) in MeCN.

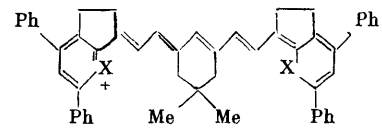
6. Spectral-luminescent properties of polymethine dyes in highly concentrated solutions

Highly concentrated solutions of the tri-, tetra-, and pentacarbocyanines (XXXII)–(XXXVI), absorbing in the region 1270–1500 nm, have interesting spectral-luminescent properties.[27,116,117] Thus, with increase in the concentration of the dye (XXXII) to 10^{-3} mol L^{-1} and above, in parallel with quenching of its principal fluorescence band at λ^{f}_{max} = 1283 nm, a new long-wave emission band is observed of approximately three times the intensity and with λ_{max} = 1613 nm.[116,117] The absorption spectrum of this compound remains unchanged for the whole working range of concentrations (10^{-5}–10^{-2} mol L^{-1}). On the basis of these data, longwave luminescence is explained by the formation and decomposition of associations of excited molecules.[116,117] In the ground state, molecules of PD (XXXII) are not associated, because the bulky phenyl groups that are present, displaced from the plane of the heteroradicals,[96] do not allow the molecules to approach sufficiently. On excitation of the pyran-2-ylcyanines and their hetero analogues, a considerable elongation of the carbon–heteroatom bonds occurs.[79,118] This decreases the steric hindrance between the heteroatoms and phenyl groups considerably. The orders of the C–C(Ph) bonds in the excited state are increased.[118] Both circumstances allow the phenyl groups to move into the plane significantly in the excited state and considerably facilitate the formation of associations.



(XXXII)–(XXXIV)

PD	*n*	*m*	R
(XXXII)	0	2	Ph
(XXXIII)	0	2	H
(XXXIV)	1	3	Ph



(XXXV), (XXXVI)

X = S (XXXV), X = Se (XXXVI).

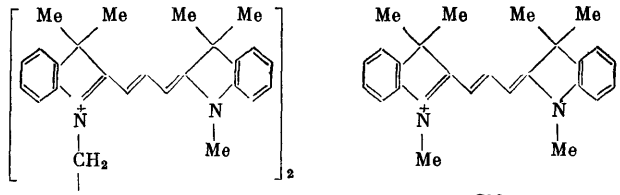
Highly concentrated solutions of PD (XXXII)–(XXXV) generate emission in the most longwave region 1400–1800 nm, with λ_P = 1060 nm.[27,117] This method should be promising for the generation of emission in the near infrared range, since it makes possible a considerable increase in both ΔS and φ. To bring about a significant increase in the quantum yield of fluorescence for monomeric organic dyes that absorb at more than 1200 nm, by means of structural changes, is highly problematical [for PD (XXXII)–(XXXVI), φ = 0.01–0.1%],[27] since small energy intervals and the effective promoting roles of high frequency CH-vibrations in this region, make internal conversion a powerful channel for the decay of electronic excitation.[44,119]

7. Spectral-luminescent properties of polymethine dyes with two chromophores

Much attention has been given recently to the investigation of spectral-luminescent properties of compounds with two chromophores,[120–123] since the intramolecular transfer of absorbed light energy from one chromophore to the other allows them to re-emit it effectively with a large red shift. Polymethine dyes with two chromophores (biscyanines) became known in 1965.[124] Fundamental relationships between the absorption spectra of PD and their chemical structure have been established.[125] Only the first steps have been taken towards the establishment of analogous relationships for the luminescence spectra of biscyanines.[126–129] Luminescence has previously been taken only as evidence for the structure of PD with two chromophores.[130,131]

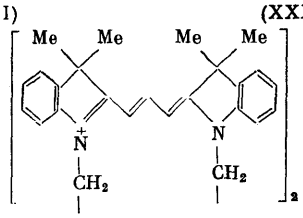
In the case of the biscyanines, resonance interaction of the chromophores, according to exciton theory,[132] causes splitting of the S_1-level into levels with higher energy S'_1 and lower energy S''_1.[125–128] In a number of cases, splitting into a *T*-level is also possible.[133] Electronic transitions $S_0 \rightarrow S'_1$ and $S_0 \rightarrow S''_1$ give rise to short- and long-wave bands respectively in the absorption spectra of biscyanines, compared to the bands associated with the $S_0 \rightarrow S_1$ transition in the monomeric (parent) dyes.[125–128] For illustration,

the spectra of the bisindocarbocyanine (XXXVII) and the parent indocarbocyanine (XXXVIII) can be compared.[128,134]



ClO_4^- (XXXVII)

ClO_4^- (XXXVIII)



ClO_4^- (XXXIX)

PD	λ^a_{max}, nm	λ^f_{max}, nm (CH_2Cl_2)
(XXXVII)	508, 570*	581
(XXXVIII)	550	570
(XXXIX)	506*, 590	662

*The more intense absorption band.

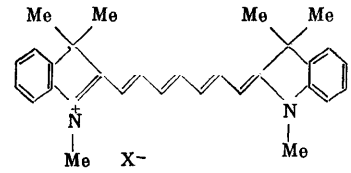
The transition $S'_1 \rightsquigarrow S''_1$ in the dimers is non-radiative.[135] Therefore, on excitation of the biscyanines, for both the short- and long-wave absorption bands, fluorescence is seen only from the S''_1-level. This situation gives rise to an increase in the shift of the emission bands relative to the shortwave absorption bands and the increase is greater, the more sharply the bands in the absorption spectra of the biscyanines move apart. According to exciton theory, the absorption bands move apart to a maximum for parallel orientations of the chromophores.[132] Therefore the change from the bis-dye (XXXVII) to (XXXIX) is accompanied by a sharp increase in the bathochromic shift of the fluorescence band relative to the short-wave absorption band.

It should, however, be borne in mind that long wave transition is forbidden for parallel orientations of the chromophores.[132–135] Luminescence occurs as a result of partial remission of the band, because of distortion of the "sandwich" structure (of the dye XXXIX) and slight displacement of the chromophores relative to each other, because they have a step-like form.[131] Therefore the luminescence of the dimers of such a structure is weak. It is also weak in the biscyanines with angular dispositions of the chromophores, for example in (XXXVII), by comparison with the monomeric PD (XXXVIII).[129] This, first of all, gives rise to an increase in the probability of intersystem crossing with change from the parent compounds to the bis-dyes.[136] This increase takes place on account of the decrease in energy difference between the S''_1 and T levels in the dimers in comparison with the S' and T levels in the monomers.

It appears to be possible to increase the luminescence of the dimers, as also of associations of some organic dyes, by the "kindling" of delayed luminescence.[137] In the dimers, it must in fact occur more easily than in the monomers, because of the increase in the probability of both $S_1 \rightsquigarrow T$ and the reverse $T \rightsquigarrow S_1$ transitions.[138]

III. The influence of the nature of the counter-ion on the spectral-luminescent properties of polymethine dyes

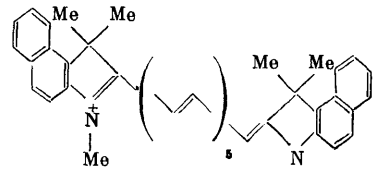
It has traditionally been thought that the spectral-luminescent properties of PD are not dependent on the nature of the colourless counter-ion but are determined only by the structure of the chromophore.[8–11] In the example of the caitonic indotricarbocyanines (XL) and (XLI) it has been shown[139] that in solvents of low polarity, as opposed to polar, the anion has a strong influence on the position, intensity and shape of the absorption bands.



(XL), (XLI)

PD	X	Solvent	λ^a_{max}, nm
(XL)	ClO_4	benzene	734*, 790
		ethanol	744
(XLI)	I	benzene	730, 790*
		ethanol	744

*The more intense band



(XLII)—(XLIV)

PD	X	λ^a_{max}, nm	λ^f_{max}, nm	τ, ps (dichloroethane)
(XLII)	I	1035	1075	97
(XLIII)	ClO_4	1035	1120	75
(XLIV)	BF_4	1035	1150	55

In the light of these published results, a wide range of investigations into the spectral-luminescent, nonlinear-optical, photophysical, and photochemical properties of cyanines in low polarity media, has subsequently been developed. On the basis of a study of ionic equilibria, the influence of salt addition, temperature, and the addition of polar ionising solvents, it was confirmed that solutions of indotricarbocyanines (XL) and (XLI) follow the Lambert-Beer law, and that the dependence of their absorption spectra on the nature of the counter-ion is caused by the formation of various types of ion pair. This conclusion was later confirmed by electroconductivity data.[140] Further investigations showed that the formation of such pairs can also give rise to marked changes in the spectral-luminescent properties of other types of salt-like PD.[141–144] A need arose to establish the structures of polymethine ion pairs.

The structures of ion pairs of dyes of the indolene and benz[*c,d*]indole series have been studied by means of ^1H, ^{14}N, and ^{15}N NMR spectroscopy[143,145,146] and by NMR with lanthanide shift reagents. It was shown for these PD that the anion is located in the

region of the nitrogen heteroradical, at which the maximum positive charge is shown, by quantum chemical calculations, to be concentrated.[143,144] On electronic excitation, a redistribution of charge occurs in the cations of the dye. Therefore the probabilities of formation of ion pairs in the ground and excited states are different. Thus, the positive charge on the cation of the pentacarbocyanines (XLII)–(XLIV) is more localised on the heteroradical in the S_1-state than in the S_0.[147] In the excited state, therefore, they form ion pairs more readily than in the ground state. Indeed, in dichloroethane, the position of the absorption band of PD (XLII)–(XLIV) does not depend on the nature of the anion. Conversely, the fluorescence band is displaced into the longwave region for the series of anions $I^- \rightarrow ClO_4^- \rightarrow BF_4^-$.[147] In this same series the values of φ and τ decrease regularly.[147]

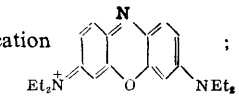
The described effects are caused by an intensification of electrostatic interactions and consequently, the formation of tighter ion pairs in the above mentioned sequence of anions in agreement with equivalent electroconductivity and dissociation constant data for pentacarbocyanines.[148] Intensification of electrostatic interactions on changing from I^- to ClO_4^- and BF_4^-, lowers the energy of the activated state,[147] and leads to a bathochromic shift of λ_{max}^{φ}.[147] In addition, the localisation of the anion at one of the heteroradicals gives rise to a disturbance of the electronic symmetry of the dye, leading to a displacement of the positive charge in this state. As a result, an alternation of bond order in the PC arises for the pentacarbocyanines (XLII)–(XLIV), and also for the asymmetric cyanines.[111] This, on the one hand, intensifies the vibrational interactions[110,111] but, on the other, increases the probability of isomerisation or, to a lesser extent, intensifies the critical vibrations around the bonds of the chain.[4] Both of these processes lead to an attenuation of the magnitude of φ and τ. Vibrational interactions and the probability of rotation about the bonds is greater, the tighter the ion-pairs that are formed. Therefore in the series of PD (XLII)–(XLIV) there is a regular decrease in the quantum yield of fluorescence and the life time of the excited state.[147]

A still greater effect on these values in low polarity media is caused by coloured organic anions, having their own system of π-bonds[149] as, for example, in the dyes (XLV), (XLVI) and (L).

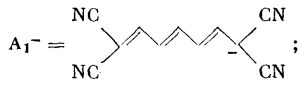
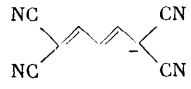
PD	Dye*	Solvent	λ_{max}^{a}, nm
(XLV)	$K_1^+A_1^+$	benzene	549, 763
(XLVI)	$K_2^+A_1^-$	,,	535, 663
(L)	$K_3^+A_2^-$	dichloroethane	448, 1030

PD	Dye*	Solvent	λ_{max}^{a}, nm
(XLVII)	$K^+{}_1C(CN)_3^-$	benzene	753
(XLVIII)	$K^+{}_2ClO_4^-$	,,	658
(XLIX)	$\overset{+}{N}(CH_3)_4A_1^-$	,,	551
(LI)	$Na^+A_2^-$	dichloroethane	448

*Designation adopted:

K_1^+ = cation of dye (XLI); K_2^+ = cation  ;

K_3^+ = cation of Pd (XLII)–(XLIV);

A_1^- =  ; A_2^- = 

Cation-anion dyes (XLV) and (XLVI) form ion-pairs in solvents of low polarity as do the corresponding cationic types.[149] In these ion-pairs, on account of the electrostatic forces of attraction, the two chromophores which have different electronic structures become "associated", in contrast to the chromophores of the biscyanines considered above. If the initial cationic and anionic dyes absorb in similar regions then the formation of a cationic-anionic compound will be accompanied by resonance interactions of the chromophores, leading to a change in the position of the electronic bands, as in the case of the biscyanines. For the cationic-anionic compounds (XLV) and (XLVI) in benzene, the absorption bands move apart: the longwave bands moving bathochromically and the shortwave bands hypsochromically, relative to the absorption bands of the corresponding cationic (XLVII), (XLVIII) and anionic (XLIX) dyes.[149]

For compound (XLVI) the absorption bands move apart to a greater extent than for (XLV), since (XLVIII) and (XLIX) absorb light at closer wave lengths than compounds (XLVII) and (XLIX).

For the cationic-anionic dye (L) there are also two absorption bands, but these do not move apart in comparison with those of the corresponding cationic and anionic cyanines.[150,151] This is due to the fact that the regions of absorption for the cationic and anionic chromophores differ sharply. Therefore resonance interactions, leading to splitting of the S_1-level and, consequently, to separation of the bands for PD (L), do not take place. Absorption bands for the cationic-anionic compound (L) are characterised by a significantly smaller integral intensity and greater width than the absorption bands of the corresponding cationic (XLII) and anionic (LI) dyes,[150,151] as the result of the formation of an ion pair, disturbing the electronic symmetry of the chromophore for the former more strongly than for the latter. Such a difference is due to the presence of a system of easily polarisable conjugated bonds and alternating positive and negative charges in the anions of cationic-anionic dyes, in contrast to the anions of the cationic types. It is able to increase the electronic asymmetry of the chromophores on account of non-resonance interactions with the analogous system of bonds of its cation and therefore cationic-anionic dyes have lower values of φ and τ than the corresponding cationic dyes.[150,151] For compound (L) in dichloroethane, τ = 49 ps, and for its analogue with the trimethineoxanine anion it falls to 24 ps.[150,151]

In polar solvents, the spectral-luminescent properties of PD (XL)–(LI) are independent of the nature of the anion, since these dyes are completely dissociated in these solvents.

Such a large reduction of τ in cationic-anionic compounds, with practically complete transparency at λ = 1060 nm, allows their use as effective passive locks for solid state lasers.[150] Cationic PD (XLII), widely known in the USSR under the number 3955 and having a large value of τ, works well in quality modulation.[152]

Cationic-anionic compounds, like mixtures of PD with other classes of dye, for example PD (II) plus rhodamine S[153] or PD (XLI) plus oxazine 750,[155] may also be used successfully for the transformation of light energy, with a large red shift. This shift, as in the case of the biscyanines, is achieved on account of the separation of the short- and long-wave bands of their ion pairs as a result of interaction of the chromophores. They are more promising than mixtures of dyes as transformers of light energy, since transfer of energy within ion pairs may occur in dilute solutions and is not dependent on the concentration of the dye, as is the case for the original components of mixtures. The latter circumstance may lead to undesirable concentration effects in mixtures of dyes.[156–158]

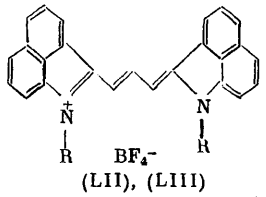
IV. Structure of associations of ion pairs of polymethine dyes

Salt-like cyanines with simple anions can also prove to be excellent transformers of light energy when they are associated. The association of PD in silver halide photographic emulsions has been widely investigated, since they have a considerable effect on the sensitising ability of cyanines in these emulsions.[10,159] Until recently, therefore, attention was given primarily to the problem of aggregation of dyes in aqueous solvents.[160] In these solutions, associations of cyanines are of low stability. They dissociate easily on warming.[161] In water and especially in other polar solvents aggregation of dyes occurs at high concentrations. This leads to concentration quenching of luminescence.[156]

Conversely, in low polarity media, cyanines easily associate in dilute solutions ($10^{-7}-10^{-5}$ molL^{-1}) at room temperature.[141,143] This is caused by the fact that the association of PD in low polarity media, in contrast to polar, comes about on account of both dispersion interactions and electrostatic interactions of different charges in the ion pairs according to the scheme $K^+A^-...K^+A^-$.[141-143]

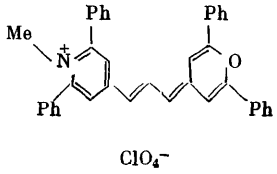
The study of association of salt-like dyes in low polarity solutions is frequently very difficult because of their low solubility. However for PD this problem can be solved by the introduction of aliphatic hydrocarbon radicals into their molecules.[143] Recently, interest in such PD has revived sharply in connection with their ability to form a Langmuir-Blodgett poly-layer,[162-170] which finds wide application in various fields of science and technology.[171]

The influence of processes of association in low polarity media on the spectral-luminescent properties of salt-like cyanines have been investigated in detail.[141-144]



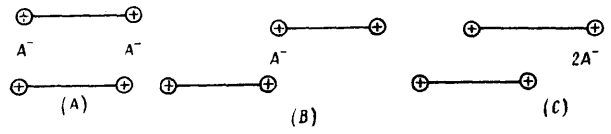
(LII), (LIII)

R = $C_{10}H_{21}$ (LII); R = $CH_3C_6H_4$ (LIII)



(LIV)

It has been shown that PD with a planar structure, not containing bulky substituents, for example (LII), easily form associations of ion pairs with a "sandwich" structure on lowering the polarity of the solution.[141-144] The formation of a "sandwich" structure favours the localisation of the anion in the region of the nitrogen heterocycle.[143] This is due to the fact that the terminal cations on both sides attach "rigidly" to the anions, because of the electrostatic attraction of the differing charges of the monomers of the ion pairs (Structure A).[143] Structure A is also advantageous from the point of view of dispersion interactions, since these are maximum for parallel orientations of the chromophores.[135] Therefore "sandwich" salt-like cyanines have high strength in low polarity media. They do not decompose on boiling even in high-boiling point, low polarity solvents,[143] in contrast to cyanines in polar, particularly aqueous, solvents.



The formation of associations with structure (A) is acompanied by a fall in the intensity of the absorption and luminescence bands of monomeric PD molecules to practically complete extinction and the appearance of new short-wave absorption bands (Fig. 4*a*, *b*). Thus for compound (LII) in low polarity media, the absorption band of its "sandwich" structure is shifted hypsochromically by 100 nm more than is the absorption band of the monomer.[141-144]

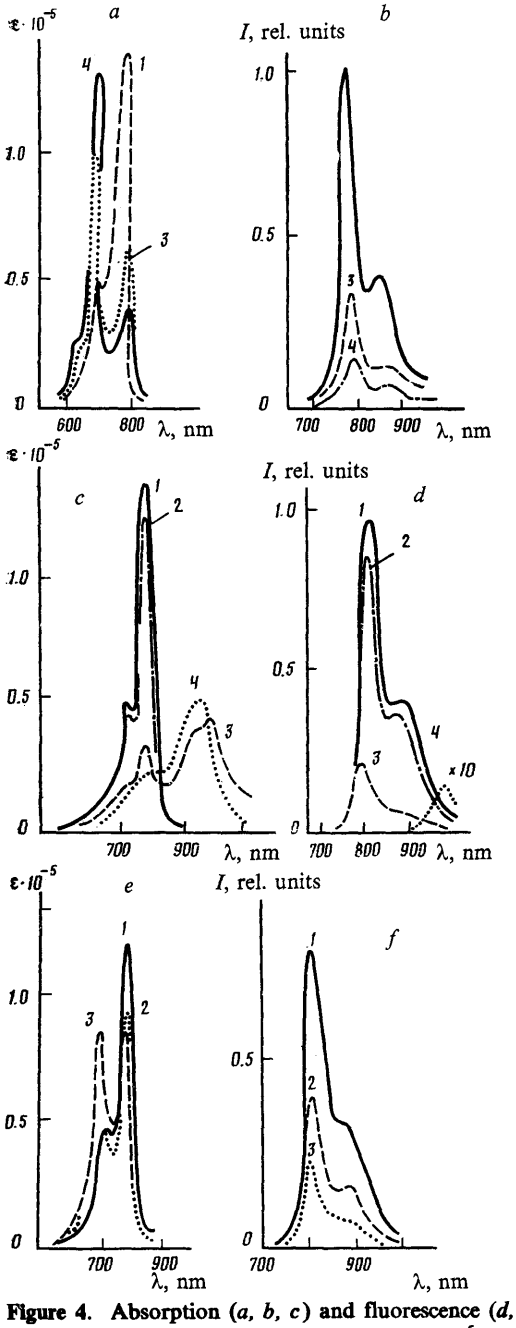


Figure 4. Absorption (*a*, *b*, *c*) and fluorescence (*d*, *e*, *f*) spectra of PD (LII) (*a*, *b*) and (LIII) (*c*–*f*) for $C = 10^{-5}$ mol L^{-1} in mixtures of CH_2Cl_2 and hexane (*a*–*d*) (CH_2Cl_2 content in %): *1*, 100; *2*, 50; *3*, 20; *4*, 10) and in DMF–water (*e*, *f*) (DMF content in %): *1*, 100; *2*, 20; *3*, 10. Fluorescence spectra standardised against the spectra of (LII) in CH_2Cl_2.

The introduction of bulky substituents hinders the formation of associations with structure (A). They are especially effective in the region of the heteroradicals, where the maximum positive charge is concentrated, since they hinder the "rigid" attachment of cations of dyes in the type (A) structure. However, in this case, it is possible for the cations to be attached at one end in a "head-to-tail" structure (Structure B), in which the angle between the direction of the chromophores is close to 180°.[143,144] The formation of associations with structure (B) is accompanied by the appearance of electronic spectra with new long-wave bands.[135,160] For example, replacement of the decyl groups in the hetero-radicals of the dye (LII) by tolyl groups (compound LIII), which deviate significantly from the plane of the chromophore, [as in the case of cyanine (XIX)] leads to the appearance of these bands (Fig. 4*c*) on reduction of the polarity of the medium (i.e. with increase in the content of hexane in the hexane–methylene chloride mixture).

The magnitude of the shift of the absorption and luminescence bands of associated molecules of PD, with respect to the corresponding bands of the unassociated molecules, deserves special attention. This magnitude is *ca.* 200 nm, which is equivalent to lengthening of the PC of the dye by two vinylene groups. Since dyes with long chains are much less photochemically stable than those with short chains, it may be hoped that associations of type (B) will be promising for the transformation of light energy from the visible into the near infrared region of the spectrum, especially as these large shifts of the electronic bands occur in even dilute solutions. This ease of association of salt-like cyanines in low polarity solutions depends on strong electrostatic attraction between the differing charges in the ion pairs of the monomers.[143,144]

It is significant, that association of the dye (LIII) in polar solutions is accompanied by opposite changes.[144] As for the cyanine (LII), in parallel with a drop in absorption ability and quenching of the luminescence, there is a characteristic appearance of a new short-wave absorption band at a distance >100 nm from the absorption band of the monomer (Fig. 4*e*, *f*). This difference depends on the fact that in polar solutions the anion does not take part in association. Under these conditions, therefore, the chromophore does not need to be so precisely fixed in the "sandwich" structure as in low polarity media. In this connection, the PD (LIII) in the DMF–water system is able to form some deformed "sandwich" structures in which the chromophores are displaced with respect to each other (structure C), on account of dispersion interactions,[144] allowing a reduction in steric hindrance between the $N-C_6H_4CH_3$ groups. Deformation of the "sandwich" structure in a DMF–water mixture is associated with greater intensity of the forbidden long-wave absorption band (Fig. 4*e*, *f*) by comparison with a solution of the same dye in a methylene chloride–hexane mixture (Fig. 4*c*, *d*).[144]

Changes in spectral-luminescent properties according to the polarity of the medium, as observed for the associated forms of compound (LIII), occur also for other PD.[172]

In low polarity media, various types of salt-like cyanines are able to associate, in particular to form dimers.[141–144] It is convenient to take advantage of this fact in those cases in which chemically bonded dimers—biscyanines—cannot be synthesised. The latter are interesting targets for use in the study of problems of chromaticity and luminescence in organic dyes, but they are frequently difficult to obtain. This is due firstly to the fact that their synthesis is accompanied by the formation of traces of monomeric dyes which are difficult to separate, especially in terms of luminescent purity. Furthermore, not all heterocycles yield bi-quaternary salts for use as starting materials in the synthesis of biscyanines.

The bis-dyes themselves associated considerably more easily than the parent dyes in low polarity solutions.[126,128] This is due to the presence of two anions in the biscyanines, so that the probability of association of their ion pairs is increased by comparison with monomeric PD.[126,128]

In polar solutions the anion does not take part in aggregation. Nevertheless, in this case, as also in low polarity solvents, biscyanines associate more easily than the parent dyes. This is due to the fact that aggregation occurs in polar solutions on account of dispersion interactions of the π-systems of the PD. For compounds with two chromophores, these systems are more extended than in those with one chromophore. The former, therefore, associate more easily than the latter.[126,127]

V. Spectral-luminescent properties of polymethine dyes in polymeric matrices

Polymeric matrices also can be regarded as low polarity media. Coloured polymeric materials are especially widely used at present in quantum electronics,[173–175] helioenergetics,[176,177] and as agents for recording information.[178,179] Polymeric matrices have a number of operational advantages by comparison with liquid media,[173–175] although these advantages may only be realised if, in addition, the spectral-luminescent properties of the dye do not deteriorate under these conditions.

The first attempt to introduce PD into polymeric matrices led to a marked distortion of their spectral-luminescent properties.[180,181] In addition, a new band appears for many PD at the short-wave end of the absorption spectrum and the intensity of the long-wave band decreases, for example in the case of thiopyranyltricarbocyanine (XXIII) when dichloroethane is replaced by poly(methyl methacrylate) (PMMA).[181–184] These changes are accompanied by the quenching of luminescence.[185] It has been shown[182–185] that the described spectral-luminescent effects are caused by the formation of ion pairs and by their association in the type (A) "sandwich" structure, in the same way as in low polarity liquid solutions.[141–143] It has also been shown that such association leads to a fall in the photochemical stability of coloured polymeric matrices.[181,183]

It is difficult to avoid the association of PD in polymers, as it is in low polarity liquids, since association occurs at even low concentrations of cyanines.[183,184] The situation is also complicated by the fact that for a number of purposes highly delicate films are required, for example for passive laser locks.[186] For achieving the required degree of transmission of such films it is necessary to use a concentration of dye that is some orders of magnitude higher than that used for measurement of the absorption spectra in a 1 cm cell.

In order to reduce the tendency of salt-like PD to the formation of ion pairs, and also therefore association, it is necessary to use polymers with high values of dielectric permeability, ε. However, the preparation of such polymers is difficult. For the majority of polymeric materials ε is <10,[187] and dyes are therefore not completely dissociated in these materials. It is possible to facilitate the dissociation of PD in matrices which have low values of ε by the use of polymers containing polar groups. The role of such groups is to solvate the charges of the chromophore of the dye, separating them from the counterions, and to some extent hinder the formation of tight ion pairs.[147] Solvent separated ion pairs have practically the same electronic spectra as the solvated ions.[148] Therefore the formation of such pairs in a polymer does not cause a substantial

change in the spectro-luminescent properties of salt-like PD from those found in liquids, even if the cyanines are fully dissociated in liquids. Specific solvation of the charges of PD by polar groups of the polymer also reduces the electrostatic and dispersion interactions between the chromophores of the dye, making association of the latter more difficult.[126,142]

For cationic PD, which undergo mainly nucleophilic solvation,[188] it is necessary to use polymeric matrices that contain strongly nucleophilic groups, for example polyvinylbutyral, polyepoxides, and polyurethanes. The latter are especially promising, since they not only have strongly nucleophilic groups (comparable in nucleophilicity to DMF), but also they also have some of the highest values of ε for polymeric media.[187] The absorption spectra of thiopyranyltricarbocyanine (XXIII) in these polymers, in contrast to PMMA which has a lower value of ε, have the same form as in liquid solvents (Fig. 5).[183,184] Conversely, in polystyrene, which is characterised by minimum values of ε and nucleophilicity *B* (both of which are comparable to those of toluene) the form of the spectral curve of the same dye is altered considerably more than it is in PMMA (Fig. 5).

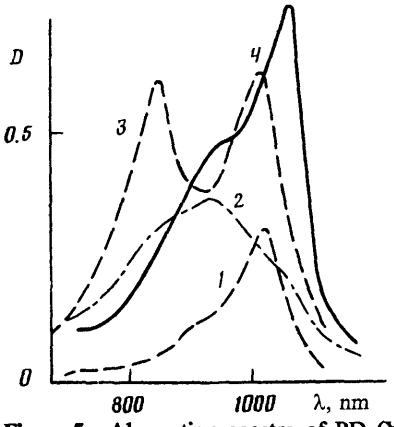


Figure 5. Absorption spectra of PD (XXIII). *1*, in dichloroethane ($C = 10^{-4}$ mol L^{-1}, *1* = 69 mm); *2*, in polystyrene; *3*, in poly(methyl methacrylate); *4*, in polyurethane (*2*–*4*, $C = 5 \times 10^{-7}$ mol g^{-1}, *1* - 70 mm).

However, a change in the nature of the matrix is not always justified. Thus, for example, for use in luminescent solar concentrators (LSC) the most preferred polymer is PMMA, which possesses excellent optico-mechanical properties[189] and is also extremely accessible and cheap.

In order to avoid the association of polymethines in PMMA, it is therefore necessary to modify them. For example, in the molecule of thiopyranyltricarbocyanine (XXIII) it is possible to introduce bulky substituents in order to prevent the formation of associations with structure (A).[185] Thus, if a hydrogen atom in the *meso*-position [dye (XXIII)] is replaced by a phenyl group [dye (XXIV)], the shape of the spectral curve remains the same in both dichloroethane and PMMA. An analogous result is also obtained with the introduction of other bulky substituents, such as CH_3, Cl, or *iso*-C_3H_7 into the *meso*-positon.[183] The formation of "sandwich" structures can be prevented, not only by the introduction of bulky groups into the polymethine chain, but also by their introduction into the heteroradicals.[183]

The above-mentioned substituents, having decreased the tendency to association of thiopyranylcyanines in polymers, substantially increased the photochemical and radiation stability of coloured matrices.[185] It allowed them to be used as the basis for the production of highy effective passive film locks, working in synchronised mode and guaranteeing the generation of ultra-short impulses of picosecond duration.[185,190]

If the association of PD in polymeric matrices is reduced to a minimum, it is possible to increase their quantum yields of fluorescence substantially. This is due to the fact that the polymer, being a "rigid" medium, impedes isomerisation processes which reduce the magnitude of φ significantly.[4] It has been shown that the quantum yields of fluorescence for a series of PD are increased more strongly by their introduction into a polymeric matrix, than by complete cyclisation of their PC. For example, on going from thiacarbocyanine (I) with an open chain to its analogue (X) with a rigidly fixed PC chain the value of φ is increased from 5 to 53%, whereas with the introduction of PD (I) into a polymer this value increases to 72%.[191]

A greater increase in the quantum yield of fluorescence of the thiacarbocyanine (I) by its introduction into a matrix, than by "chemical" fixing of its chain, is most probably due to the fact that not only are isomerisation processes hindered in "rigid" media, but also the quenching of luminescence, due to diffusion-controlled collision with molecules of oxygen and other quenching impurities, is decreased.[192–194] This fact also leads to a significant rise in the photochemical stability of coloured polymeric matrices based on PD. The latter are, in fact, able to sensitise the formation of singlet oxygen,[192–194] which is one of the basic factors in the photochemical destruction of cyanines.[195–197] In a polymer, because of weak diffusion, the generation of singlet oxygen is of low probability and cyanines are therefore more stable in these than in liquid solutions.

In luminescent ability and photochemical stability many PD in polymeric matrices are comparable with a wide range of luminophores, such as rhodamine 6G, POPOP, and various coumarins, etc.[198] In matrices, therefore, even those cyanines which are unsuitable as active laser media in liquid solutions can be used for the highly effective generation of emission.[199] In a polymer, the effectiveness of generation of emission is increased not only because of the increase in φ, but also as the result of a decrease in the losses that are caused by the induced absorption of the isomer in the intensified band.[200]

It should be noted that in "rigid" media the Stokes shift frequently falls. Thus, for the pyridylpyranyltetracarbocyanine (XXXI), which has one of the highest ΔS values, the Stokes shift decreases by 820 cm^{-1} on going from acetonitrile solution to polyurethane film, although its magnitude nevertheless remains rather significant. In general, if a decrease in ΔS occurs in polymers, then it does not decrease to the same extent as for completely fixed PC, with saturated cyclic groupings.[191] Small values of ΔS are also characteristic of other classes of structurally rigid luminophores.[198]

The possibility of achieving large Stokes shifts and quantum yields of fluorescence, together with high photochemical stability, makes coloured matrices based on PD more promising than the above named luminophores for the solution of problems connected with the transformation of light energy. One of these is helioenergetics.[191,201] The use of PD as LSC has been proposed.[191,201] It was shown that cyanines, that are not even the most suitable, can have larger coefficients of energy concentration than the widely used rhodamine 6G.[191,202]

It should be emphasised that a considerable increase in φ can be achieved, not only by the introduction of PD into polymeric matrices but also by increasing the viscosity of the medium.[59,60,203,204] It has therefore been possible to produce highly effective fluorescent probes, based on polymethines, for the determination of the microviscosity of phospholipid membranes.[205]

It was recently found that a sharp increase in the quantum yield of fluorescence of PD can also occur in low viscosity aqueous solutions in the presence of DNA.[206] This fact is of particular interest, since quenching of luminescence normally occurs in water because of the high tendency of PD to aggregation especially with the formation of "sandwich" structures, under these conditions.[156,160] Furthermore, the concentration of DNA employed does not increase the viscosity of the solution sufficiently for this be the cause of an appreciable increase in φ. The role of DNA in the case decribed is different. On the one hand, DNAs are surface active substances which hinder the association of dyes in aqueous solutions,[207] but on the other they form complexes with molecules of PD, most probably on account of electrostatic interactions which fix the dye rigidly in one isomeric form only. If this form is the *trans*-isomer, which usually has good luminescence, then fluorscence of the cyanine is enhanced in the presence of DNA. Conversely, in the case of the *cis*-isomer, quenching occurs.[4] Depending on the type of DNA and PD the formation of one or other of isomer occurs and, consequently, the enhancement or quenching of luminescence. Polymethines can therefore be used successfully in aqueous solutions as fluorescent probes for the recognition of types of DNA.[206]

VI. Influence of the nature of the solvent on the spectral-luminescent properties of polymethine dyes

It has been generally accepted that the solvent cannot have a significant effect on the spectral-luminescent properties of salt-like PD, since in contrast to intraionic (merocyanine) dyes, their dipole moment should change little on excitation.[208,209] It has been shown[34,110,111,188] that cyanines, depending on their chemical structure, may undergo strong solvation that becomes distinctly apparent from the position, intensity, and form of the electronic bands. For the exact quantitative estimation of these changes the moments method is applied,[210,211] as used in probability theory for the determination of functional parameters of various distributions, for example intensities in absorption and luminescence spectra.[210,211]

This method was used to calculate the mean frequencies (centres of gravity) of the bands ($\bar{\nu}$), oscillator strengths (f), band widths (σ), coefficients of asymmetry (γ_1), excess (γ_2), and fine structure (F). The magnitude of $\bar{\nu}$ has an advantage over the band maximum, in that its position in the series becomes determined more precisely and it more strictly characterises the vertical change in energy.[210] The magnitude of σ, being proportional to the dispersion of the band, allows an objective comparison of the widths of curves of different shapes to be made, in contrast to the half-widths (widths at half height) that are traditionally used for these purposes. The coefficients γ_1, γ_2, and F give additional information relating to changes in symmetry, steepness, and the degree of fine structure that is observed with widening or narrowing of the spectral curves. It has been shown possible to use these coefficients for analysis of the mechanisms of broading (uniform or otherwise) of the electronic bands.[211]

Moments of the absorption bands are determined by the coordinates ε/ν, and of the fluorescence bands by the coordinates W/ν^4, since these coordinates follow the law of mirror symmetry for the named spectra most exactly.[212]

1. Solvatochroism

In the examples of the dyes (XL) and (LIV), which differ sharply in chemical properties and in the regions of absorption and shape of their spectral curves, a study was made of the influence of various parameters of solvent polarity on the position, intensity, and shape of the absorption bands.[188] For this purpose the same range of solvents were used, that made it possible to obtain objective information on the influence of intermolecular interactions on the spectroluminescent properties of dyes. For a series of solvents with similar properties it was concluded[213] that a change in the position of the absorption band maximum for symmetrical cyanines correlates well with the Bayliss refractive index function: $(n_D^2-1)/(2n_D^2+1)$. However the inclusion of even a small number of solvents of other types at once led to a breakdown of the relationship,[214] i.e. the correlation is only satisfactory for a series of solvents of the same type.[214] Indeed, as seen for the example of the indotricarbocyanine (XL) (Fig. 6) neither ν^a_{max} (correlation coefficient $r = 0.912$) nor $\bar{\nu}^a$ ($r = 0.807$) correlate with the mentioned Bayliss function if different classes of solvent are used. The picture is not improved substantially by the use of the two-paramter function $f(n_D, \varepsilon)$.

Hence it follows, that solvation of the PD cations depends not only on macro- but also on microscopic properties of the medium. It has been shown for cyanines of the types (XL) and (LIV), and in general for polymethines that do not contain functional groups able to form hydrogen bonds, that the microscopic properties are determined by specific electrostatic interactions of the charges of the PD molecules and the solvent.[188] On the basis of an analysis of solvatochroism effects for cyanines (XL) and (LIV) and their dependence on empirical parameters of solvent polarity. viz. nucleophilicity (B) and electrophilicity (E), it was established for cationic PD that these interactions are significantly more sensitive to changes in parameter B than E. In other words, specific solvation of these dyes is determined mainly by nucleophilic solvation of the positive charges of their cations with the negative charges of the solvent molecules. Specific solvation becomes stronger with increasing unevenness in the distribution of charge in the cyanine molecules[34] and this in its turn increases with lengthening of the PC, deviation of the electron-donating abilities of the terminal heterocyclic groups from average values,[34,215] and increase in the electronic asymmetry.[111] Thus, for thiapentacarbocyanine (V), containing two benzthiazole nuclei, the electron-donating ability of which is above average, replacement of weakly nucleophilic methylene chloride by strongly nucleophilic DMF gives rise to such marked changes in the absorption spectra, that they do not appear to be caused by the change in the nature of the solvent but by the presence of two different dyes (see Fig. 1*a*). Equally strong effects, with change in the nucleophilicity of the medium, are observed for cyanines having weakly electron-donating radicals.[216] In both cases these effects are shown more distinctly for PD with longer PC (see Fig. 1).

It has been established that the nucleophilicity of a solvent has a significantly greater influence on the shape of the band (especially width), than on its position. The latter is more sensitive to change in the refractive index of the medium.

On the basis of an analysis of the moments of the absorption bands of PD in pairs of solvents, for which one parameter of

polarity was the same but the other different, the following law was formulated[188] concerning the influence of the solvent on the characteristics of the absorption bands of these dyes: in order to maximally deepen the coloration, to narrow the band and to increase the peak intensity, it is necessary to use, as media, solvents which have as large refractive indices as possible (a necessary condition for deepening of the coloration) and as low nucleophilicities as possible. Conversely, the largest increase in coloration, widening of the bands, and decrease in their extinction occurs in solvents with maximum B (a necessary condition for the creation of wide bands) and minimum n_D.

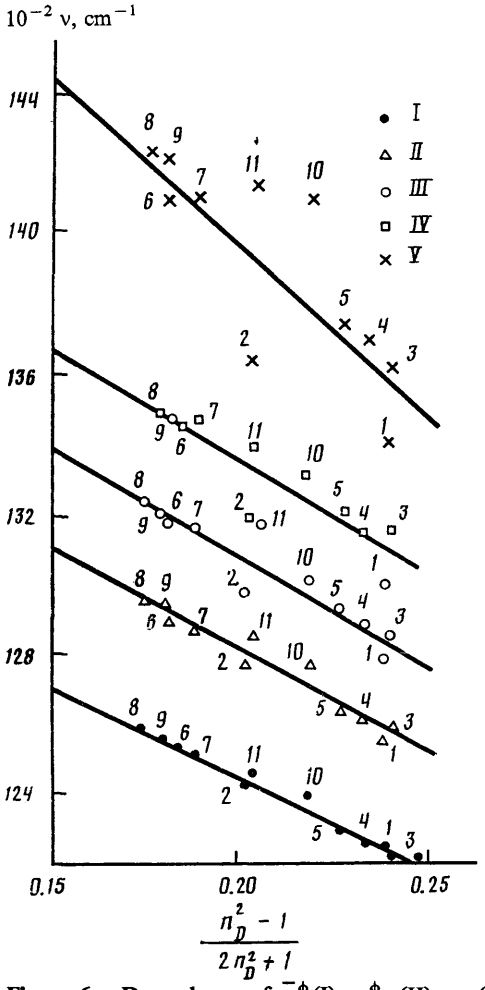


Figure 6. Dependence of $\bar{\nu}^{\Phi}$(I), ν^{Φ}_{max}(II), ν_{00}(III), ν^{a}_{max}(IV), and $\bar{\nu}^{a}$(V) for the dye (XL) on the Bayliss function. *1*, *o*-dichlorobenzene; *2*, methylene chloride; *3*, nitrobenzene; *4*, benzonitrile; *5*, pyridine; *6*, ethanol; *7*, nitromethane; *8*, acetonitrile; *9*, acetone; *10*, DMSO; *11*, DMF.

2. Solvatofluorochroism

The first report of the solvatofluorochroism of cyanines appeared only in 1987.[217] In this publication, and subsequently in others,[38,211] the influence of the nature of the solvent on the moments of the fluorescence bands of PD (XXVI), (XXXVIII) and (XL) was investigated. It was shown that the magnitudes of solvatofluorochroism effects were significantly less than those of solvatochroism. For example, the replacement of *o*-dichlorobenzene by DMF (these solvents differ considerably in the magnitude of n_D and B)[188] leads to a hypsochromic shift of the maximum and mean frequencies of the fluorescence bands of indotricarbocyanine (XL) of 400 and 361 cm^{-1} respectively, whereas the analogous values for absorption are 470 and 818 cm^{-1}. Still more contrasting is the influence of the solvent on the magnitudes of α^{a} and σ^{f}. Thus, in the above mentioned pair of solvents, the change in band width in the emission spectra amounts to only 58 cm^{-1} but in the absorption spectra to 414 cm^{-1}.[38,217] It was shown that the solvent has very little effect on the shape of the fluorescence band, in contrast to that of absorption, even for the strongly solvatochromic thia- (see Fig. 1*b*) and thio-pyranylcyanines with log PC. It has been found that the magnitudes of σ, γ_1, γ_2 and F for fluorescence bands are significantly less than the corresponding values for the absorption bands (especially σ).[211,217] This shows that the law of mirror symmetry for absorption and emission spectra is not observed. This conclusion is fairly important, since it was traditionally considered from the appearance of the spectral curves, that the above mentioned law is observed for the cyanine (XL) and for many other PD.[68,69] Only the application of the moments method revealed the considerable deviation from this law.

Deviation from mirror symmetry, and also a decrease in the magnitude of solvatofluorochromic effects by comparison with solvatochromic, witnesses to a weakening of the solvation of dyes in the excited state by comparison with the ground state.

From the data obtained by quantum chemical calculations for the molecule of indotricarbocyanine (XL), it follows[217] that the charges in the S_1-state have, as a rule, smaller numerical values than in the S_0-state. The total positive charge responsible for nucleophilic solvation also decreases with excitation (in the ground state it is 1.616 and in the excited state, 1.324).[217] In the excited state, therefore, electrostatic interactions (nucleophilic solvation), in contrast to dispersion interactions, must become significantly weaker, causing a decrease in the solvatofluorochromic effects by comparison with the solvatochromic.

With electronic excitation of the cyanine cations a marked redistribution of charge occurs. Specifically solvated forms of the dyes (SSFD), which are formed on account of nucleophilic solvation in the ground state, will therefore become unstable in the excited state and will seek to undergo reorganisation, with some dissociating completely. The probability of formation of SSFD in the excited state also falls because of a decrease in the absolute magnitude of the majority of the charges in this state by comparison with the ground state. As a result, the solvent will have a smaller effect on the shape of the absorption band than on the fluorescence band. Weakening of nucleophilic solvation leads also to a large decrease in the magnitudes of σ^{Φ}, γ_1^{Φ}, γ_2^{Φ} and F^{Φ}, by comparison with σ^{a}, γ_1^{a}, γ_2^{a} and F^{a},[211] giving rise to deviation from mirror symmetry.

Additional narrowing of the fluorescence bands, by comparison with the absorption bands and a decrease in the influence of the solvent on the magnitudes of σ^{Φ}, γ_1^{Φ}, γ_2^{Φ} and F^{Φ}, occurs because of radiationless, directed transfer of light energy from the "blue" to the "red" solvate.[218,219] As a result, not all SSFD take part in such a transfer in emission in contrast to absorption, but mainly long-wave and non-specific solvates, absorbing in the still more "red" region than SSFD.[38,217]

The occurrence of radiationless directed transfer of energy also accords with the fact that quantum yields of fluorescence and life-

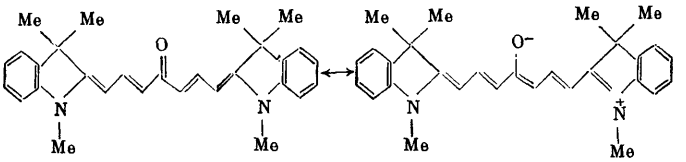
times of the excited states in a group of strongly nucleophilic solvents are, as a rule, lower than in weakly nucleophilic solvents,[38] since the probability of the formation of SSFD and, consequently, degradation of the excitation energy of the former is higher. This is due to the fact that the quantum yield and life time depend not only on the nucleophilicity of the medium, but also on its other properties, for example on viscosity. Therefore, in the highly viscous DMSO, in spite of its high nucleophilicity, a fairly high quantum yield of fluorescence is achieved.[38]

In alcohols, for PD absorbing in the region >1000 nm, the value of τ is minimal.[220] This is because there are additional routes of degradation for the energy, as a result of an overlap of the long-wave absorption bands of the cyanines with the overtone bands of the valence vibrations of the alcoholic OH groups. By deuteriation of these alcoholic groups, the magnitude of τ increases. Thus, for thiopyranylcyanine (XXIV), the values of τ in C_2H_5OH and C_2H_5OD are 14 and 23 ps respectively.

The Stokes shifts increase in almost the same way in a series of solvents, as the band widths. This is explained by the fact that ΔS is caused by an increase in hypsochromic band shifts, which result from a large reduction in the energy of the ground state of the dye, by comparison with the excited state, on account of an increase in nucleophilic solvation of the former.

This solvation is so significant, that the characteristic positions of the absorption bands, as already noted, do not correlate satisfactorily with the Bayliss function of refractive index (Fig. 6). This is specially clear for $\bar{\nu}^a$ since the average frequency, being at the centre of gravity of the band, is extremely sensitive to changes in band shape. A change in the latter, under the influence of solvent, is due mainly to specific rather than general electrostatic interactions, leading to a breakdown of the correlation mentioned above. Solvatochromic shift of the band maxima is more dependent on the polarisability of the solvent, than on its nucleophilicity. There is therefore an approximate correlation (r = 0.912) between ν^a_{max} and the Bayliss function. The picture is improved to some extent by the closeness of the 0−0 transition, ν_{00} (Fig. 6). This is because the vibrational transition corresponding to the band maximum, is partially removed under the influence of solvent because of the formation of SSFD.[221] The extent of this removal changes according to the nature of the solvent. Therefore the band maximum, in contrast to the magnitude of ν_{00}, may be dependent in different solvents on various vibrational transitions in a sub-level of the excited state of the SSFD. But in spite of the advantage of the closeness of the 0−0 transition, a satisfactory correlation between this and the refractive index function is not acheived (r = 0.942). This once again shows the significant contribution of specific interactions in solvated cationic dyes. Indeed, a satisfactory relationship of the above mentioned characteristics of the electronic bands and refractive index is only obtained for uncharged compounds.[222,223] The excellent correlation shown between $\bar{\nu}^\Phi$ and the refractive index (r = 0.993) for fluorescence of the dye (XL) is therefore striking; it is better than for ν^a_{max} (r = 0.974), although the latter is extremely satisfactory. These facts convincingly confirm the conclusion that nucleophilic solvation is significantly weakened in the exicted state, in comparison with the ground state.

The opposite is true of the analogue of dye (XL), indotricarbo-ketocyanine (LV).[224,225]

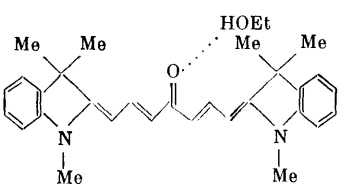


(LV)

(LV): λ^a_{max} = 465 nm; λ^f_{max} = 475 nm (heptane).

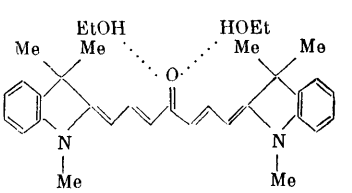
Compound (LV), being intra-ionic, is shown as a nonpolar-bipolar borderline structure. The latter predominates in the excited state. Therefore in the molecule (LV) in the S_1-state, in contrast to the cationic indotricarbocyanine (XL), the specific electrostatic interactions are intensified. This is shown by the fact that an increase in the nucleophilicity of the medium does not give rise to a bathochromic shift rather than a hypsochromic shift, as takes place for compound (XL).[224] Such changes in the spectra are caused by the fact that nucleophilic solvation of the ketocyanine (LV) increases in the excited state and reduces its energy more than for the ground state.

In the S_1-state of compound (LV), electrophilic solvation is also increased. This becomes especially apparent in protic solvents, in which the ketocyanine (LV) forms two types of complex (LVa) and (LVb).[224,225]



(LVa)

(LVa): λ^a_{max} = 487 nm; λ^f_{max} = 540 nm



(LV6)

(LVb): λ^a_{max} = 565 nm; λ^f_{max} = 620 nm.

The probability of their formation is increased in the excited state, since the negative charge on the oxygen atom increases on excitation. This leads to a rise in ΔS in protic solvents by comparison with aprotic. In addition, there is an excellent increase in the order of the quantum yield. This is caused by saturation of the carbonyl with hydrogen bonds, leading to an increase in rigidity of the complexes, fixed in the all *trans*-conformation.[225]

Owing to the high values of ΔS and φ, alcoholic solutions of ketocyanines generate emission effectively with both laser[226] and lamp[227] pumping.

VII. Conclusion

PD are seen to possess unique and widely ranging spectral-luminescent properties.

Depending on structure, cyanines may absorb and luminesce in the whole visible and near infrared regions of the spectrum. At the present time, PD have the most interesting long-wave (1600 nm)[1] $\pi-\pi^*$ transitions among all the dyes investigated, with extinction reaching 5.10^5 l mol^{-1} cm^{-1}.[126]

Band shape may change from being strongly structured to being completely diffuse, from the most narrow ($\sigma \leqslant 700$ cm^{-1})[126,215] to the most wide (σ 3000 cm^{-1}).[115]

The quantum yield of fluorescence and the life-time lie within the limits 0.01–100% and $10^{-12}-10^{-9}$ s respectively.[3,4] Stokes shifts change from unity to 100 nm (from 200 to 7000 cm^{-1}).[112,115]

The spectral-luminescent properties of some PD are strongly sensitive to change in the nature of the medium, and others significantly so.[34,216]

No one class of organic dyes possesses such contrasting properties. Furthermore, a change from one class to another, is not always accompanied by such strong effects. PD are therefore ideal subjects for answering the main question of photoluminescence, formulated by S I Vavilov as follows: "...why does one molecule luminesce and others not?".[228] Further investigations of the spectral-luminescent properties of cyanines and the factors which determine them, should answer this question to a large extent. Special attention will be given to non-radiative processes in the region > 1000 nm, since only PD show interesting absorptions in this region. It will assist in the simple resolution of the question of the roles of internal conversion and high frequency vibrations in processes of deactivation of the excited states of the molecules.

Their solution may be most facilitated by the preparation of fully deuteriated PD with $\lambda^{a}_{max} > 1000$ nm. Since, in this region, the gap between the S_1- and T-levels decreases, an increase in the role of triplets in deactivation of the excited state can be expected. Elucidation of their role in deactivation is very necessary for the creation of stable PD which absorb and luminesce in the near infrared region. Singlet oxygen luminesces in this region (λ^{ϕ}_{max} = 1270 and 1590 nm).[119] PD with $\lambda_{max} > 1000$ nm should therefore occupy a fundamental place in the study of problems of energy transfer from themselves to singlet oxygen and *vice versa*. As a result of such a study, effective quenchers and sensitisers for singlet oxygen may be discovered.

In future, much greater attention will apparently be given to the investigation of the spectral-luminescent properties of the highly excited state of PD. Practical applications of cyanines are, in fact, frequently based on interactions of their molecules with intensive light fields. Such interactions give rise to non-linear optical effects in molecules of PD, with the participation of highly excited states.[229] Until recent times, the study of the latter was very difficult because of their very short life times. However, with the appearance of multi-photon laser spectrosocpy[230] this aim has become practicable for PD.[231]

Investigations in all these areas will make it possible to search still more effectively and purposefully for cyanines that are suitable for the solution of the problems of the transformation of light energy.

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