ACTIVE LASER MEDIA BASED ON POLYMETHINE DYES

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The prospects for preparing active laser media for the near-IR range based on polymethine dyes are considered. General ways of optimization of the fluorescence quantum yield, Stokes shifts, bandwidths, and lasing efficiency as functions of polymethine structure and solvent nature are analyzed. It is shown that asymmetric polymethine dyes are most promising for generation in the near-IR range.

Many problems connected with sensing of the atmosphere and ocean call for efficient conversion of wavelengths of widely used laser pump sources λ_p of the UV (308 and 337 nm) and visible (510, 532, 578, and 694 nm) ranges into the near-IR range of spectrum.[1,2] For this conversion, the dyes with a large Stokes shift (SS), high fluorescence quantum yield (φ), and wide absorption bands are required.[3] Aryl methane and arylamine dyes widely used as active media have small SSs.[4] Moreover, long-wave boundary of amplification of their spectrum lies in the range 700–750 nm.[4] Its shift toward red wavelengths is rather problematic. From this viewpoint, more promising are symmetric polymethine (cyanine) dyes (PDs) for which intense absorption can be obtained at the longest (among organic dyes) wavelengths.[4] However, symmetric PDs also have small SSs and narrow absorption bands. As a result, it is difficult to excite efficient generation for $\lambda > 800$ nm when $\lambda_p < 600$ nm. Therefore, we tried to increase their SSs and absorption bandwidths (σ).

One of the methods for solving this problem is introduction of π-substituents in heteroradicals.[5] For example, substitution of phenyl (PD2) for the ethyl groups of the PD1 or, what is still better, of the hetaryl (PD3) results in the increase of SS, φ, and σ.
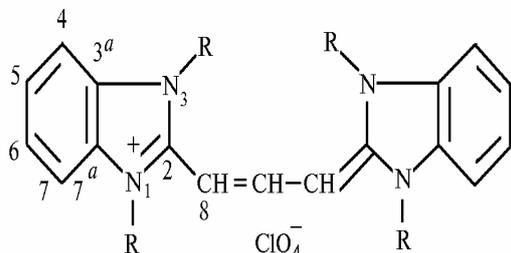
PD1: R = Et, SS = 600 cm^{-1};
PD2: R = Ph, SS = 1245 cm^{-1};
PD3: R = Py, SS = 2000 cm^{-1}.

The increase of φ due to the π-substituents decreases the probability of formation of (*cis-* or *trans-*) stereoisomers because of weighting of the PD molecules

by these substituents. Deformation vibrations of substituents, in our opinion,[5] broaden the absorption and fluorescence bands of PDs.

The increase of SS was interpreted in Ref. 4. In the ground state, phenyl (pyridyl) groups of PD2 and 3 are largely eliminated from the matrix chromophore plane due to steric hindrances formed by hydrogen atoms in the 4, 4′, 7, 7′, and 8, 8′ states. In the excited state, as follows from the results of quantum chemical calculations, the bonds N_1C_2, N_3C_2, C_4C_{3a}, and C_7C_{7a} are strongly elongated.[4] This decreases the steric hindrances for the rotation of phenyl groups; as a consequence, they may significantly flatten upon excitation. Their flattening will be also favored by the increased orders of the bonds NPh in the excited state.

Flatter structure of phenyl-(pyridyl) substituted PD2 and 3 in this state (in comparison with the ground state) leads to larger bathochromic shifts in the fluorescence spectra than in the absorption spectra. Therefore, the transition from PD1 to PD2 and 3 is accompanied by the increase of SS. Introduction in the PD molecules of π-substituents capable of flattening leads not only to the increase of SS, but also to the decrease of the generation threshold and the increase of the efficiency of conversion.[5] Nevertheless, their introduction permits to solve the formulated problem only partly, because SS and σ increase insignificantly for radiation conversion from the wavelengths shorter than 600 nm into the IR range.

The significant increase of the Stokes shifts and broadening of the cyanine bands may be achieved by introduction of substituents in mesostates branching CDs, that is, leading to the formation of the trinuclear PDs.[6] Their SS and σ significantly increase the analogous characteristics of the dinuclear PDs.

Such a strong effect is caused by the fact that upon excitation the trinuclear PDs, in contrast with the dinuclear ones, significantly change their geometry. In the ground state, the first type of dyes has the propeller-shaped structure, while in the excited state each from the bunches is alternately oriented perpendicular to the plane of two others.[6] However, the increase of SS and σ of the trinuclear PDs is

accompanied by the sharp decrease of φ. This is connected with the fact that their complanarity is destroyed and band alternation is much stronger manifested in PCs than in the corresponding dinuclear PCs.[6] As a result, BB and conformation processes are intensified for the first PCs in comparison with the second PCs. As a consequence, the trinuclear PDs fluoresce much more weakly than dinuclear PDs. Therefore, the former are not promising for preparation of the active media.

Large values of SS and significantly high φ can be achieved for some PDs with the help of inversible photochemical reactions of photon transport.[7] This would allow us to obtain generation in the 720−810 nm band at $\lambda_p = 530$ nm (see Ref. 7). Photochemical reactions with proton transport are very sensitive to small variations of the pH of the medium and occur only in few PDs. These circumstances limit their wide use for preparation of the active laser media.

In some cases, good results on shifting of the generation band toward the near-IR range of spectrum may be obtained using dye mixtures[8] (as a long-wave component of PD) or chemically bounded compounds formed on their basis, namely, bifluorophores.[3] This approach is justified for significantly overlapped absorption acceptor and donor fluorescence bands and high value of φ of the latter. These circumstances limit severely the use of these systems for obtaining generation.

In Ref. 9 the feasibility of colossal shift of the absorption and fluorescence bands toward the longer wavelengths was demonstrated by the formation of associations of PD ion pairs with an angle of 180° between the chromophores. These associations, according to the exciton theory, have only a long-wave band in the electron spectra with bathochromic shift from the monomer band.[9] Thus, PD4 of methylene chloride has $\lambda^a_{max} = 780$ nm and $\lambda^f_{max} = 810$ nm, whereas its aggregate of ion pairs in the mixture of methylene chloride with 90% hexane has $\lambda^a_{max} = 950$ nm and $\lambda^f_{max} = 995$ nm.


PD4
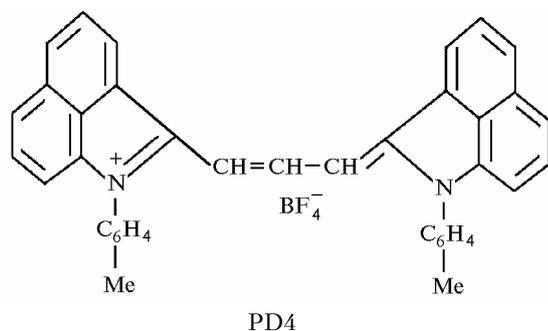
Formation of associations with an angle of 180° between the chromophores of this dye is favored by the tolyl groups attached to nitrogen atoms. They, as in PD2, are eliminated from the chromophore plane due to the steric hindrances and due to this, hinder the

formation of the sandwich ion pairs by virtue of specific cyanine construction more favorable for them.[4] Really, substitution of the tolyl group of PD4 by less voluminous alkyl group under the same conditions gives 100% sandwich with $\lambda^a_{max} = 679$ nm (see Ref. 9). It is essential that the absorption and luminescence band shift of PD4 association from the monomer bands is 200 nm, which is equivalent to PD elongation by two vinyline groups. Unfortunately, luminescence of these associations is rather weak due to intensification of intercombination conversion in the process of aggregation of dyes.[4] For the same reason, the values of φ are also small for chemically bounded dimers − biscyanines.[4] These circumstances still hinder the efficient use of associations of polymethines and biscyanines for preparation of active laser media.

The increase of the Stokes shifts and quantum yields of fluorescence can be obtained for ketocyanines in proton donor solvents.[10] Here, ketocyanine forms two types of complexes − PD5a and PD5b.

PD5a: $\lambda^a_{max} = 487$ nm, $\lambda^f_{max} = 540$ nm.
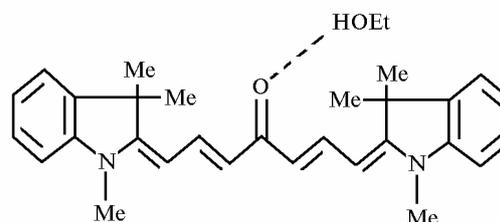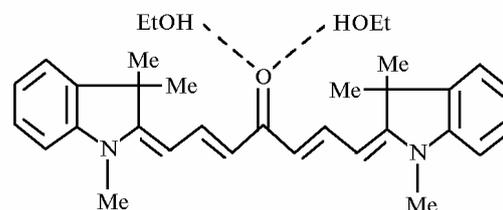
PD5b: $\lambda^a_{max} = 565$ nm, $\lambda^f_{max} = 670$ nm.

Probability of their formation is increased in the excited state, because the negative charge on the oxygen atom is increased upon excitation. This leads to the increase of SS in comparison with proton dyes ($\lambda^a_{max} = 465$ nm and $\lambda^f_{max} = 475$ nm in heptane). In addition, φ increases approximately by an order of magnitude. This is caused by carbonyl saturation by hydrogen bonds leading to the increase of rigidity of complexes and *trans*-conformation fixing everywhere.[10] Owing to large SS and φ, ketocyanines in alcohol solutions generate efficiently in the 620−650 nm wavelength range with laser[11] and flash lamp[12] pumping. However, the compounds of PD5a(b) type, capable of converting the radiation into the near-IR range, are lacking now.

An interesting phenomenon is established for highly concentrated solutions of tri-, tetra-, and pentacarbocyanines[13,16] that absorb light in the 1270−

1500-nm wavelength range. Thus, when the PD6 concentration exceeds 10^{-3} mole/l, along with quenching of its fundamental fluorescence band with $\lambda^f_{max} = 1283$ nm, a new more intense (approximately three times) and longer-wave radiation band appears with $\lambda^f_{max} = 1613$ nm (see Ref. 14). The absorption spectrum of this compound remains unchanged in the entire working range of concentrations $10^{-5} - 10^{-2}$ mole/l. A radiation beam has a narrow angular divergence. Its spectral composition depends on detuning of the cavity length. On the basis of these data, it is speculated that long-wave luminescence is connected with processes of four-photon parametric interaction. In this case, the Stokes wave of the scattered radiation with frequency ν_s is generated as a result of nonlinear interaction of the running electron polarizability lattice with excited dye molecules.[14] It is likely formed as a result of interference of pump and superfluorescence fields with the frequencies ν_1 and ν_2 ($\nu_1 > \nu_2$), respectively. This is accompanied by bathochrome shift of ν_s (in nm) according to the relation $\nu_s = 2\nu_1 - \nu_2$ (see Ref. 14).


PD6
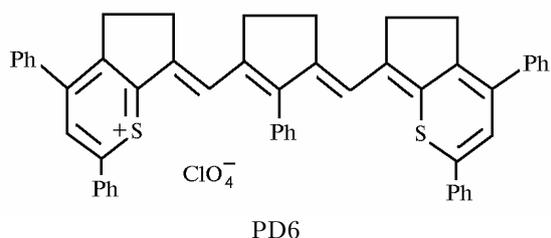
The generation in longer wavelength range 1400–1800 nm at $\lambda_p = 1060$ nm[13] was excited in highly concentrated cyanine solutions. This method should be promising for obtaining generation at wavelengths >1200 nm, because it significantly increases not only SS, but also φ. It also should be noted that the significant increase of the quantum fluorescence yield of monomer organic dyes absorbing in this range by way of structural changes is rather problematic.[3] This is caused by the fact that at wavelengths >1200 nm, because of small energy interval and efficient promoting role of high-frequency CH vibrations, the internal conversion is a powerful channel for electron excitation degradation. Therefore, even at $\lambda_p = 1060$ nm the generation obtained for symmetric cyanines for wavelengths >1000 nm is inefficient.[15]

Up to now, the above-described phenomenon in highly concentrated PD solutions has been observed only for wavelengths >1200 nm and for the narrow class of cyanines. Its nature has not yet been adequately understood. Therefore, a search for PDs capable at high concentrations to produce new bands of luminescence with larger Stokes shift and to generate radiation in the near-IR range at $\lambda_p = 308, 337, 510,$ and 578 nm is difficult.

Spectral luminescence characteristics of asymmetric PDs are more suitable for the solution of

this problem.[16–18] In the ground state, its charge is significantly shifted toward electron donor (basic) heteroradical (its shift the greater, the stronger is the electron dye asymmetry[16]). For example, total charges of benzimidazole and benzothiazole radicals of PD7 differ more than twice[16] (0.8583 and 0.3877, respectively). As a result of this charge shift typical of asymmetric PD in comparison with symmetric ones, soltvatochromism is intensified and alternation of band orders takes place from heteroradical to heteroradical resulting in deviations (deviation is a quantitative measure of electron asymmetry), decay of vinylene shifts, and broadening of bands in their absorption spectra.[10] In the excited state the pattern is sharply changed.[17,18] Thus, the changes of the above-mentioned PD heteroradicals became practically equal (total charges are 0.6401 and 0.6309, respectively). This significantly decreases the alternation of the band orders.[17,18] Hence, in the excited state even typical electron asymmetric dyes approach to symmetric ones. Therefore, in the fluorescence spectra of the former, in contrast with the absorption spectra, deviations are practically absent, vinylene shifts (≈ 100 nm) remain constant, as in symmetric PD, and the band profiles remain narrow, universal, and independent of the nature of the solvent.[17,18] Because the light absorption in cyanines occurs for the ground state geometry and emission − for the excited one,[19] such a great difference in the electron structure of these states of the asymmetric PD engenders large Stokes shifts. Salient features of spectral luminescence characteristics of asymmetric cyanines permit to prepare on their basis promising active media for the near-IR range,[20] which have the following advantages.

PD7
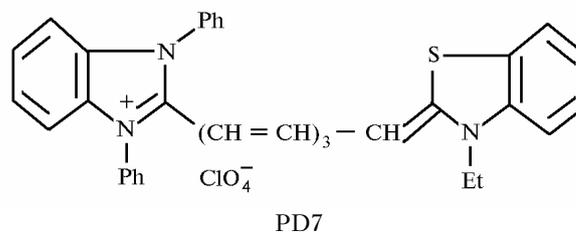
First, for asymmetric cyanines such large σ can be obtained that the band of one of such PDs practically encompasses all visual range of the absorption spectrum. This makes it possible, in contrast with the symmetric cyanines, coumarins, rhodamines, and other dyes widely used for generation[4,21] to use one asymmetric cyanine as an active medium for several pumping sources with significantly different λ_p (see Ref. 20). Second, asymmetric PDs have SS largest among organic dyes (575 nm (7670 cm^{-1}, see Ref. 22)). Therefore, they are capable of re-emission of the absorbed light energy from short-wave range of spectrum to the IR range almost inaccessible for other generating organic dyes. Third, significant broadening of absorption bands and increase of the Stokes shifts of them can be obtained for fairly high quantum yields of

fluorescence.[17,18]   Fourth, the values of σ and SS of asymmetric PDs can be varied in a wide range by selection of the solvent.

Broadening of the absorption bands and the increase of the Stokes shift can be realized easy due to the increase of the electron asymmetry of PD by virtue of the increase of the difference between the number of electron donors of end groups and elongation of PC (see Ref. 4). Polymethines of type 7 generate efficiently in the near-IR range (efficiency no smaller than 15%) at λ_p = 308, 510, 532, 578, and 694 nm (see Ref. 20). For wide practical application, a set of highly efficient asymmetric PDs has been prepared. Their use as active laser media permits one, for example, to saturate the optical transitions of the K, Rb, Cs, and He atoms in the 760–900-nm wavelength range which, in its turn, can be used to solve various geological and ecological problems[1,2,23] with the help of low-power lasers without additional amplifying cascade.

REFERENCES

1. V.V. Fadeev, D.K. Bunin, and P.S. Venedictov, Kvant. Elektron. **23**, No. 11, 963–973 (1996).
2. V.H. Zakharov, O.K. Kostko, L.N. Birich, et al., *Laser Sensing of the Atmosphere from Space* (Gidrometeoizdat, Leningrad, 1988), 213 pp.
3. A.A. Ishchenko, Kvant. Elektron. **21**, No. 6, 513–534 (1994).
4. A.A. Ishchenko, *Structure and Spectral-Luminescence Characteristics of Polymethine Dyes* (Naukova Dumka, Kiev, 1994), 232 pp.
5. O.V. Przhonskaya and E.A. Tikhonov, Opt. Spektrosk. **44**, No. 3, 480–485 (1978).
6. Yu.L. Bricks, A.A. Ishchenko, A.D. Kachkovski, and A.I. Tolmachev, Dyes and Pigments **8**, No. 2, 353–369 (1987).
7. O.V. Przhonskaya, E.A. Tikhonov, F.A. Mikhailenko, and L.I. Shevchuk, Zh. Prikl. Spektrosk. **37**, No. 1, 54–60 (1982).
8. L.K. Denisov, E.D. Belega, and B.M. Uzhinov, Elektron. Tekh. **11**, No. 4, 38–56 (1988).
9. A.A. Ishchenko, F.G. Kramarenko, A.G. Moydannic, et al., J. Inf. Rec. Mater. **19**, No. 2, 207–219 (1991).
10. V.V. Danilov, G.G. Dyadyusha, and A.A. Rykov, Zh. Fiz. Khim. **58**, No. 4, 919–924 (1984).
11. V.V. Danilov, A.S. Eremenko, Ya.T. Mazurenko, et al., Kvant. Elektron. **4**, No. 1, 195–198 (1977).
12. A.V. Aristov, V.V. Danilov, L.K. Denisov, et al., Opt. Spektrosk., **43** No. 5, 945–948 (1977).
13. H.S. Polland, T. Elsaesser, A. Seilmeier, et al., Appl. Phys. **B32**, No. 1, 53–57 (1983).
14. V.A. Babenko and A.A. Sychev, Tr. Fiz. Inst. Akad. Nauk **214**, 144–155 (1991).
15. V.A. Babenko and A.A. Sychev, Kvant. Elektron. **23**, No. 5, 413–416 (1996).
16. A.A. Ishchenko, V.M. Zubarovskii, G.A. Gromova, and N.A. Derevyanko, Zh. Organ. Khimii **23**, No. 3, 621–630 (1987).
17. A.A. Ishchenko, V.A. Svidro, and N.A. Derevyanko, Opt. Spektrosk. **71**, No. 3, 457–461 (1991).
18. A.A. Ishchenko, N.A. Derevyanko, and V.A. Svidro, Dyes and Pigments **19**, No. 3, 169–177 (1992).
19. A.A. Ishchenko, V.A. Svidro, N.A. Derevyanko, et al., Opt. Spektrosk. **66**, No. 6, 1302–1306 (1989).
20. M.V. Bondar, N.A. Derevyanko, G.G. Dyadysha, et al., Kvant. Elektron. **11**, No. 3, 462–471 (1984).
21. B.I. Stepanov, N.N. Bychkov, L.V. Levshin, et al., Pris'ma Zh. Tekh. Fiz. **14**, No. 7, 653–656 (1984).
22. A.A. Ishchenko, Zh. Prikl. Spectrosk. **55**, No. 5, 717–724 (1991).
23. V.S. Letokhov, ed., *Laser Analytic Spectroscopy* (Nauka, Moscow, 1986), 317 pp.