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INFLUENCE OF SOLVENT POLARITY AND VISCOSITY ON NONRADIATIVE PROCESSES IN OLIGOTHIOPHENES WITH INTRAMOLECULAR CHARGE TRANSFER*

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By the methods of luminescence, picosecond spectroscopy, and quantum-chemical calculations the mechanisms of electron excitation energy deactivation in some oligothiophenes with intramolecular charge transfer depending on the solvent polarity and viscosity have been investigated. While for 2-N-piperidino-5-(2′,2′-dicyanovinyl)thiophene (PDCVT) the main channel of nonradiative deactivation is the transition to a lower intermediate state with a "twisted" double bond controlled by the medium viscosity, in the case of (E)-{2-[2-5-piperidino-2-thienyl]-6-(trifluoridemethyl)-4H-4-pyranylidene}propanedinitryl (PTFDN) fluorescence quenching is initiated by the solvent polarity. For two other oligothiophenes, 2-N-piperidino-5-cyanothiophene (PCT) and 2-N-piperidino-5″-cyanoterthiophene (PCTT), differing in the length of the thiophene chain, we have revealed, along with the effective quenching of fluorescence in short-chain PCT (independent of the solvent polarity and viscosity), an increase in the radiation capacity in PCTT with increasing polarity of the solvent. The possible mechanisms of nonradiative deactivation in the investigated oligothiophenes are discussed.

Keywords: *fluorescence, change transfer, polarity, viscosity, fluorescence quenching.*

Introduction. Conjugate oligothiophenes (OT) are known as one-dimensional electron-conductive systems with a high photo- and thermostability [1], and organic polymers based on them are being widely investigated with the aim of developing various optoelectronic devices for generating and detecting optical radiation (light-emitting diodes, microlasers, wide-format displays, photodiodes, solar batteries, etc.) [2–4]. In the last few years, the attention of researchers has been focused on OTs with limit electron-donor and electron-acceptor substitutes in which effective intramolecular charge transfer (CT) from the electron-donor to the electron-acceptor part of the molecule along the chain of thiophene rings occurs. Such compounds are characterized by a marked difference between the dipole moments in the ground (μ_g) and singlet-excited (μ_e) states and exhibit, in a number of cases, pronounced nonlinear-optical properties [5].

The mechanisms of the photophysical and photochemical processes proceeding in systems with charge transfer after the absorption of a light quantum are highly diverse and depend on the chemical structure of substances, their aggregate state, and the nature of the environment. At the present time, there are divergent points of view about the mechanism of charge transfer in electron-excited electron-donor-acceptor (EDA) molecules [6–9]. The most illustrative example of this is such a relatively simple molecule as *para*-dimethylaminobenzonitryl (DMABN), which in the last forty years has been serving as a model compound for investigating processes with charge transfer. However, in the literature the discussion about the structure of the excited fluorescent state is still going on. It is believed [7] that a polar solvent in this case stabilizes the fluorescent state with charge transfer resulting from the rotation of the dimethylamino group about the single bond by 90° (the so-called TICT-state). In [8, 9], the fluorescence from the ground state

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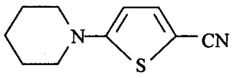
with charge transfer is attributed to either the structure of the DMABN molecule with a cyano group bent by 120^{o}C (RICT-state) [8] or the structure of DMABN with planar hybridization sp^2 of the nitrogen atom in the dimethylamino group (PICT-state) [9]. However, the singlet-excited state of molecules with intramolecular charge transfer does not always exhibit fluorescence and we have to assume its effective nonradiative deactivation [6]. In the EDA molecule, the photoisomerization processes that are effective, for example, in stilbene-like EDA molecules can compete with the charge transfer processes [10]. The diversity of phototransformation processes and the necessity of taking into account their structural features initiate further experimental and theoretical studies of the photodynamics of systems with charge transfer.

In the present work, we have investigated the spectroscopic and photophysical properties of solutions of a number of newly synthesized thiophene-containing EDA molecules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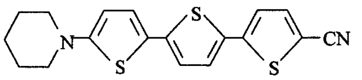
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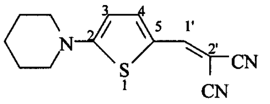
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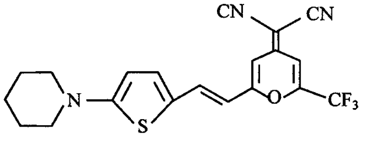

PTFDN

and performed quantum-chemical calculations of their spectroscopic and electrophysical characteristics. The EDA OT presented can be subdivided into two structurally differing groups: compounds 2-N-piperidino-5-cyanothiophene (PCT) and 2-N-piperidino-5″-cyanoterthiophene (PCTT) with a different number of thiophene rings (n = 1 and 3), as well as 2-N-piperidino-5-(2′,2′-dicyanovinyl)thiophene (PDCVT) and (*E*)-{2-[2-(5-piperidino-2-thienyl]-6-(trifluoridemethyl)-4*H*-4-piranylidene}propa- nedinitryl (PTFDN) having a central double bond but different electron-acceptor substitutes. Note that PDFDN has a high value of the quadratic polarizability $\beta = 2.6 \cdot 10^{-28}$ ESU units at a wavelength of 1.9 μm [11].

Experimental Technique and Procedure of Quantum-Chemical Calculations. The PTFDN and PDCVT synthesis is described in [11, 12], and PCT and PCTT were synthesized according to the following scheme:

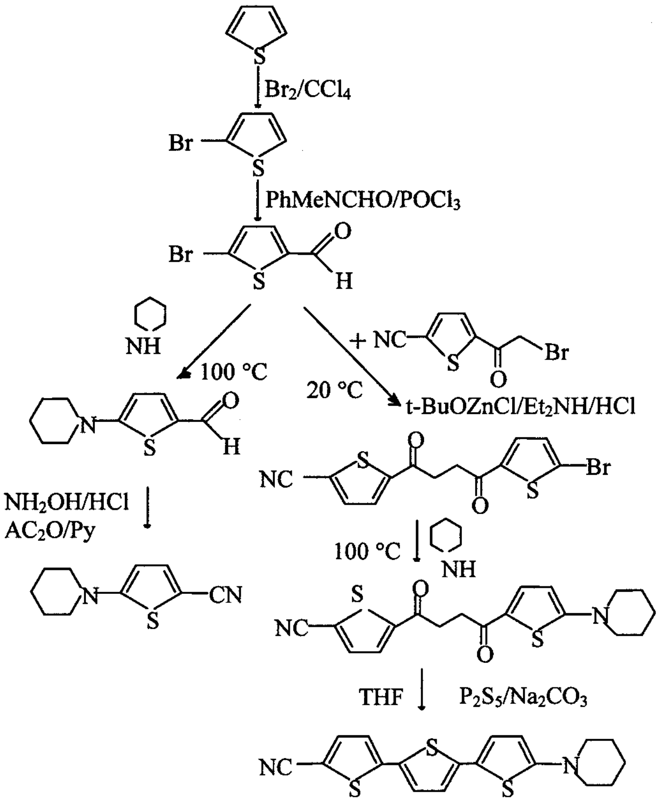


TABLE 1. Spectral-Luminescent Properties of OTs at 293 K

Solvent	λ^a_{max}, nm	λ^f_{max}, nm	$\Delta\nu_{St}$, cm^{-1}	τ_f, nsec	Φ_f
PCT					
n-Hexane	317	–	–	≤0.001	$\leq 10^{-6}$
n-Propanol	328				
PCTT					
n-Hexane	425	505	3730	1.5	0.48
Acetonitryl	435	645	7370	3.3	0.87
PDCVT					
Ethanol	464	488	1060	0.004	0.0006
Diethylene glycol	473	492	815	0.004 (0.06)	0.004
PTFDN					
Benzene	558	640	2300	1.2	0.28
Acetonitryl	567	710	3560	0.02	0.004

The PMR spectrum ($CDCl_3$, 200 MHz; δ, ppm; *J*, Hz; m, multiplet, d, doublet) of PCTT: δ = 1.60–1.82, m (6H), 3.11–3.23, m (4H), 5.98, d (*J* = 4, 1H), 6.87, d (*J* = 4, 1H), 8.94, d (*J* = 4, 1H), 7.06, d (*J* = 4, 1H), 7.14, d (*J* = 4, 1H), 7.52, d (*J* = 4, 1H) and of PCT: δ = 1.52–1.80, m (6H), 3.14–3.30, m (4H), 5.94, d (*J* = 4, 1H), 7.30 (*J* = 4, 1H). The IR spectrum for both compounds in CCl_4 is characterized by the stretching vibration frequency of the C≡N bond of 2220 cm^{-1}.

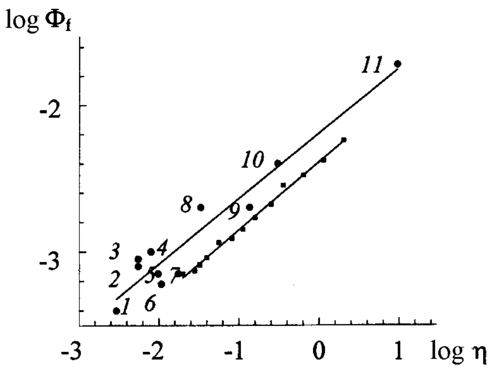
Reagent-grade solvents were purified by standard methods. Spectral-fluorescent measurements were made on the high-transmission set described in [13]. The quantum yield of fluorescence Φ_ϕ was measured by the relative method and as standards, solutions of cresyl violet dyes in methanol (F_f = 0.54 [14]) and 3,6-diaminophthalimide in ethanol (F_f = 0.6 [15]) were used. The kinetics and the spectra of induced absorption and amplification from the excited S_1 state were recorded on a picosecond spectrometer [16]. Excitation was carried out by the second harmonic of a neodymium laser (λ_{exc} = 528 nm) with a pulse duration of 4 psec and probing — by a picosecond continuum. The time characteristics in the nanosecond time interval (>1 nsec) were recorded on a PRA 3000 fluorimeter operating in the photon-counting regime.

Low-temperature measurements were made in a cryostat, where the temperature was varied by blowing liquid nitrogen vapors. A temperature-sensitive element in the form of a DS-1A silicon diode was used. The accuracy of maintaining the temperature was ±1.0 K. For low-temperature measurements, vitrifying *n*-propanol systems and an EPA mixture (diethyl ether + isopentane + ethyl alcohol in a 5:5:2 ratio) were used. The changes in the refractive index of EPA with decreasing temperature were taken into account by the relation from [17], and the temperature dependence of the change in the *n*-propanol viscosity was taken from [18].

The molecule geometry was optimized by the PM3 quantum-chemical method [19]. The ZINDO/S method [20] was employed to calculate the energies of electron transitions and their oscillator strengths. The dipole moments in the ground and excited states were calculated by the PM3 semiempirical method on the basis of the HyperChem 6.0 (HyperCube Inc.) software.

Results and Discussion. *PCT* and *PCTT* markedly differ from each other in their spectral and photophysical properties (Table 1).

For instance, the absorption spectra of PCTT at room temperature are shifted to the long-wave region from the PCT spectra, which is explained by the more extended π-conjugate system in the case of PCTT. We should note the considerable Stokes shift ($\Delta\nu_{St}$) between the absorption and fluorescence spectra of PCTT in polar solutions (7570 cm^{-1} in methanol), which can be attributed to the fact that for PCTT the change in the dipole moment $\Delta\mu = \mu_e - \mu_g$ is greater. The $\Delta\mu$ value for PCTT determined by the Lippert equation [12] proved to be equal to 27.2 D, i.e., with



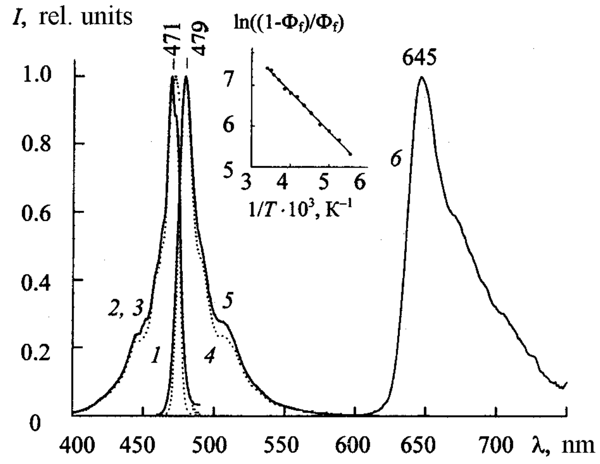


Fig. 1. Dependences of the quantum yield of fluorescence (Φ_f) of PDCVT on the viscosity of solvents (η) at T_{room} (upper straight line) [1) *n*-hexane; 2) methanol; 3) toluene, 4) dimethyl formamide; 5) carbon tetrachloride; 6) ethanol; 7) *n*-propanol; 8) formamide; 9) ethyleneglycol; 10) diethyleneglycol; 11) glycerol] and on the viscosity of *n*-propanol at various temperatures (lower straight line).

Fig. 2. Absorption (1), fluorescence (4, 5), phosphorescence (6), and fluorescence excitation (2, 3) spectra of PDCVT in EPA (1–5) and *n*-propanol (6) at 77 K; λ_{exc} = 471 (4), 445 (5), and 467 nm (6), λ_{rec} = 505 (2) and 475 nm (3); in the inset — the Arrhenius dependence for the logarithm of the nonradiative probability on the inverse temperature.

regard for μ_g = 8.4 D calculated for the ground state the dipole moment in the relaxed singlet-excited S_1 state μ_e = 35.6 D. Thus, an increase in the dipole moment for PCTT by 27.2 D in the S_1 state leads to a $0.33\bar{e}$ shift throughout the length of the molecule (~17 Å) from the electron-donor piperidine to the electron-acceptor cyano group.

The most significant difference between PCT and PCTT showed up in investigating the photophysical characteristics. For instance, for PCT we did not manage to detect fluorescence at room temperature; for it $\Phi_f \le 10^{-6}$. Under the same conditions for PCTT in acetonitryl $\Phi_f = 0.87 \pm 0.05$ and in *n*-hexane — 0.48 ± 0.03. One would expect the opposite result, because in nonpolar *n*-hexane the fluorescence spectrum is shifted to the short-wave region from the spectrum in acetonitryl by 140 nm, and accordingly, the higher-lying S_1 state of PCTT in *n*-hexane should be characterized by a smaller internal conversion constant. Therefore, in this case it may be suggested that such a polar solvent as acetonitryl stabilizes the polar PCTT molecule in the excited state by means of specific interactions and thus decreases the probability of rotary motions in a long, flexible molecule leading to nonradiative deactivation. In so doing, the fluorescence durations were 3.3 ± 0.1 and 1.5 ± 0.1 nsec, respectively. At 77 K these parameters did not change markedly. Unlike DMABN [7], for PCTT no dual fluorescence in polar solutions was detected.

PDCVT. The electronic absorption spectrum is characterized by an intense long-wave band in the visible region. The molar extinction coefficient at the absorption band maximum at 464 nm in ethanol is $6.2 \cdot 10^4$ liters/mole^{-1}·cm^{-1}, i.e., the transition is allowed. The absorption spectra of PDCVT feature a bathochromic shift with increasing solvent polarity. For instance, on passing from *n*-hexane (λ_{max} = 441 nm) to ethanol the spectral shift is 1120 cm. The fluorescence spectra of PDCVT are shifted to the long-wave region from the absorption spectra by 1625 ± 70 cm^{-1} in *n*-hexane and by 1060 ± 50 cm^{-1} in ethanol, i.e., in polar solvents the shift of the spectra to the long-wave region is weaker than in nonpolar solutions.

The quantum yield of fluorescence Φ_f of PDCVT increases linearly with increasing viscosity of the solvent (Fig. 1), changing from 0.0004 ± 0.0001 in *n*-hexane (viscosity η = 0.0029 P at 298 K) to 0.019 ± 0.02 in glycerol (η = 9.45 P at 298 K). At room temperature in the solid matrix of polymethylmetacrylate (PMMA) $\Phi_f = 0.027 \pm 0.002$. The linear dependence of Φ_f on η for PDCVT in *n*-propanol (Fig. 3, lower straight line) was also observed in

TABLE 2. Energies (ΔE) and Oscillator Strengths (f) of Transitions (ZINDO/S) and Dipole Moments in the Ground (μ_g) and Excited (μ_e) States (PM3) for PDCVT as a Function of the Angle of Rotation (φ) of the Cyano Groups about the 1′–2′ Bond

φ, deg	ΔE, cm^{-1} (nm)	f	μ_g, D	μ_e, D
0	26,101(383)	0.912	7.01	9.95
10	25,982(385)	0.914	7.04	9.94
20	25,613(390)	0.917	7.11	9.87
30	24,950(401)	0.915	7.21	9.71
40	23,898(419)	0.895	7.34	9.37
60	20,006(500)	0.709	7.89	8.17
80	11,329(883)	0.242	9.09	7.20
90	430(23,275)	0.000	15.68	7.04

the case where the solvent viscosity increased with decreasing temperature of the solution. At 77 K in the EPA mixture $\Phi_f = 1.00 \pm 0.05$. Thus, Φ_f increases 2500 times on passing from *n*-hexane at 298 K to EPA at 77 K.

It should be noted that the solvent polarity did not influence Φ_f. Indeed, in methanol and toluene, solvents differ so widely in permittivities (32.6 and 2.4) but having equal viscosities, the quantum yields of fluorescence coincide (Fig. 1).

Since the absorption spectra of PDCVT in *n*-propanol remain practically unaltered with a change in the temperature in the 293–180 K range, it may be suggested that the probability of fluorescence radiation k_f in this range does not change either. Then, proceeding from the Arrhenius linear dependence for the logarithm of the probability of nonradiative transitions $k_{nr} = k_f(1 - \Phi_f)/\Phi_f = \Sigma A_n e^{-E_A/RT}$ on inverse temperature $1/T$ (Fig. 2, inset), we can determine the activation energy E_A of the processes of nonradiative transitions, which was measured to be 7.9 ± 0.2 kJ/mole. This value is in good agreement with the data obtained in investigating the mechanism of nonradiative processes of *trans*-stilbene in various solvents [22]. It may be suggested that the nonradiative process in the PDCVT molecule in liquid solutions is also associated with the rotation about the 1′–2′ bond in the excited state. As a result of such a rotation, the molecule goes to the lower "twisted" state, in which, under the action of the polar solvent, the conformation with intramolecular charge transfer is stabilized or, as in the case of stilbene, the double bond acquires the character of a single bond and the electronic integration is minimum. The energy of such states sharply decreases to provide an effective nonradiative exchange of the electron excitation energy.

The absorption, fluorescence, and phosphorescence spectra of PDCVT at 77 K narrow and acquire a vibrational structure (Fig. 2, curves 3–6). For instance, in the absorption spectrum in the short-wave region a maximum at 445 nm appears and in the fluorescence spectrum, symmetrically to it, a maximum at 505 nm is positioned. The energy gap between the 0–0 band in the absorption spectrum (Fig. 2) at 471 nm and the vibrational satellite at 445 nm is 1180 ± 50 cm^{-1}, and in the fluorescence spectrum — 1170 ± 50 cm^{-1}. Thus, there exists a mirror symmetry between the absorption and fluorescence spectra of PDCVT in both the frequencies and intensities. The phosphorescence spectrum of PDCVT in *n*-propanol at 77 K (Fig. 2, curve b) is similar in form to the fluorescence spectrum and its maximum lies at 645 nm. The fluorescence excitation spectrum coincides with the $S_1 \leftarrow S_0$ absorption spectrum. The distance between the maxima of the fluorescence and phosphorescence spectra is 5400 cm^{-1} and the triplet energy level of PDCVT is 15,500 cm^{-1}. The spectral data for PDCVT at 77 K suggest the presence in the solution at a low temperature of one conformer, whose structure undergoes no special changes in the ground and excited singlet and triplet states.

To determine the electron transition energy for the PDCVT molecule with cyano groups rotated about the 1′–2′ bond, we have performed quantum-chemical calculations, which have shown (Table 2) that the transmission energy, the oscillator strength, and the dipole moment depend on the angle of rotation of the cyano groups about the 1′–2′ bond. The changes are especially significant at rotation angles larger than 60^o.

From Table 2 it is also seen that the transition energy decreases with increasing angle of rotation about the 1′–2′ bond and at 90^o it is equal to 430 cm^{-1}. These data agree with the above suggestion that the energy of the in-

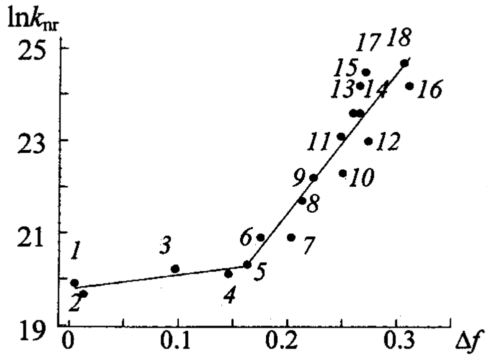


Fig. 3. Dependence of the logarithm of the nonradiative deactivation rate constant k_{nr} on the solvent polarity function Δ*f*. The k_{nr} values were calculated from the equation $k_{nr} = k_r(1 - \Phi_f)/\Phi_f$ at $k_r = 1.7\cdot 10^8$ sec^{-1}, $T = 293$ K; 1) benzene; 2) toluene; 3) dibutyl ether; 4) chloroform; 5) diethyl ether; 6) toluene + DMSO (90:10); 7) tetrahydrofuran; 8) toluene + DMSO (80:20); 9) toluene + DMSO (75:25); 10) amyl alcohol; 11) toluene + DMSO (50:50); 12) *n*-propanol; 13) toluene + DMSO (25:75); 14) diethylene glycol; 15) dimethyl sulfoxide (DMSO); 16) methanol; 17) ethyleneglycol; 18) acetonitryl.

termediate excited state decreases at rotation about the "double" bond and, accordingly, the probability of nonradiative transitions increases.

PTFDN. As opposed to the previous compounds, for PTFDN a strong fluorescence quenching with increasing solvent polarity has been revealed. Figure 3 shows the dependence of the logarithm of the nonradiative deactivation rate constant k_{nr} of PTFDN on the solvent polarity function Δ*f* [21]:

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1},$$

where ε and *n* are the permittivity and the refractive index of the solvent. The small slope in the dependence of ln k_{nr} on Δ*f* is indicative of a low quenching efficiency and is observed in low-polarity solvents (toluene, benzene, chloroform, diethyl and dibutyl ethers). With further increase in Δ*f* the fluorescence quenching efficiency sharply increases. Such a trend of the dependence of ln k_{nr} on Δ*f* can be explained by the existence of two states: a weakly polar state (with a small intramolecular charge transfer) and a strongly polar state (with a significant charge transfer). The second state stabilizes mostly in polar solvents, and in weakly polar solvents emission occurs from the weakly polar excited state. In so doing, the dipole moments of the polar and nonpolar states can differ widely. For example, for such a known dye as neutral red the dipole moments of these states are 17.5 and 4.8 D, respectively [23].

It is necessary to note the deviations from the general linear dependence in Fig. 3 for a number of polar proton-containing solvents (10 — amyl alcohol, 12 — *n*-propanol, 16 — methanol). This fact can be attributed to the ability of these solvents to interact with a fluorophore molecule, i.e., form a complex with a hydrogen bond. The specific interaction thereby leads to a decrease in the polarity of the excited complex fluorophore + solvent and, as a consequence, to a decrease in the nonradiative deactivation rate constant k_{nr} (see Fig. 3).

The radiative rate constants calculated from the absorption spectra on the basis of the approximate equation [24]

$$k_r^{abs} = \frac{\nu_0^2 \varepsilon_{max} \Delta\nu_{0.5}}{3.5\cdot 10^8}$$

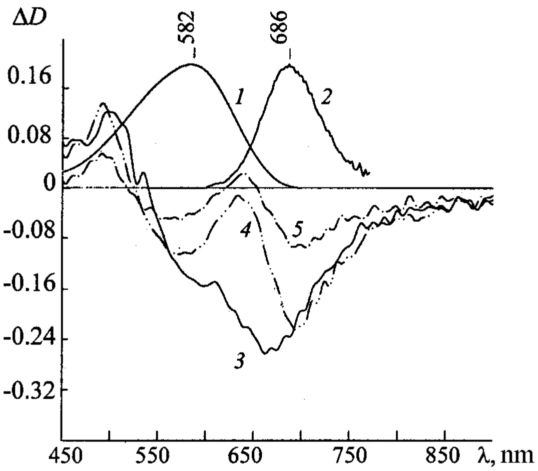


Fig. 4. Stationary absorption (1) and fluorescence (2) spectra and nonstationary spectra of PTFDN in *n*-propanol at 293 K. The fluorescence spectrum 2 was recorded at λ_{exc} = 560 nm. The time delays are 8 (3), 90 (4), and 160 psec (5).

(ν_0 and ε_{max} are the wave number and the molar decimal absorption coefficient at the absorption-band maximum and $\Delta\nu_{0.5}$ is the absorption-band half-width in cm^{-1}) and from the experimental data on the lifetimes τ_f and quantum yield Φ_f of fluorescence

$$k_r^{em} = \frac{\Phi_f}{\tau_f},$$

within the measurement error are independent of the solvent nature and their mean value is $(1.7 \pm 0.3) \cdot 10^8$ sec^{-1}. This fact indicates that the long-wave absorption band of PTFDN is formed by one electron $S_1 \leftarrow S_0$ transition and the processes of long-wave absorption and fluorescence are associated with the S_1 state alone.

With the aim of investigating the spectral-kinetic properties of the S_1 state of PTFDN in a polar solvent, we made picosecond measurements of the spectra of this OT in *n*-propanol at various delay times after the pulse excitation (Fig. 4). With increasing delay time the amplification bands (curves 3–5) shift into the long-wave region (from 665 nm at Δt = 8 psec to 700 nm at Δt = 160 psec) and the bleaching bands — into the short-wave region (from 600 to 565 nm). It should be noted that the stationary fluorescence (curve 2) and fluorescence excitation (not shown) spectra of PTFDN in *n*-propanol at 293 K remain unchanged in both the shape and the position at different excitation and recording wavelengths, i.e., the observed changes in the time-resolved amplification and bleaching spectra are associated with the excited S_1 state.

We revealed an interesting fact of a hypsochromic shift of the bleaching spectra of PTFDN in *n*-propanol with increasing delay time Δt: at Δt = 160 psec the dynamic Stokes shift $\Delta\nu_{St}$ = 3415 cm^{-1}. For comparison, in the case of the stationary fluorescence and absorption spectra $\Delta\nu_{St}$ = 2600 cm^{-1}. Thus, the time-resolved amplification and bleaching spectra of PTFDN in *n*-propanol are characterized by a Stokes shift increasing with time. This points to the fact that the molecular system displays a marked spectral inhomogeneity and consists of a set of absorbing and emitting centers with time-varying surroundings from the solvent molecules. Inhomogeneity also appears in the kinetic characteristics of PTFDN and consists of the fact that the kinetics of the intermediate processes of PTFDN in *n*-propanol are characterized by different decay times depending on the recording wavelength. For instance, in amplification spectrum recording, the decay time increases with increasing λ_{rec} (43 psec at 660 nm and 93 psec at 700 nm). Similar changes in the fluorescence decay kinetics at various λ_{rec} were also observed for phthalimides [25] and coumarin [26] in alcohols in investigating their nanosecond [25] and subpicosecond solvation relaxation [26].

Conclusions. On the basis of the obtained experimental and theoretical data for the investigated OTs the following conclusions can be drawn.

The photophysical properties of PCT and PCTT strongly depend on the chain length. For instance, in the PCT molecule (n = 1) practically the whole of the electron excitation energy (≥99%) is deactivated by means of internal conversion. In the case of PCTT (n = 3), an increase in the solvent polarity leads to an increase in Φ_f, and in acetonitryl $\Phi_f = 0.87$. We associate this fact with the stabilization of the singlet-excited PCTT molecule by the polar solvent due to the specific interactions and the corresponding decrease in the probability of nonradiative transitions through rotary motions in a long, flexible molecule.

The effective nonradiative deactivation of the electron excitation energy of PDCVT in low-viscosity solvents at room temperature is due to the transition of the molecule from the singlet-excited state to the intermediate lower state with a "twisted" conformation (about the 1′–2′ bond) from which a nonradiative transition to the ground state occurs. An increase in the solvent viscosity increases the activation barrier for the transition to this intermediate state, as a result of which the quantum yield of fluorescence for the PDCVT molecules increases and at 77 K in EPA it is equal to unity. In this case, the solvent polarity plays no important role.

In the case of the PTFDN molecule, the main state responsible for the nonradiative process is the state with charge transfer, whose energy decreases with increasing polarity of the solvent. The PTFDN molecule polarized in the S_1 state features a large dynamic Stokes shift caused by the time-varying inhomogeneous surroundings of the polar solvent.

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