Fluorescent aggregates of cation-anionic polymethine dyes with simple structures

Kh. S. Dzhulibekov,[a] A. S. Tatikolov,[b]* R. Kh. Dzhumadinov,[a] N. Nizamov,[a] and Zh. A. Krasnaya[c]

[a]A. Navoi State University of Samarkand,
15 Universitetsky bulvar, 703004 Samarkand, Uzbekistan.
[b]N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156
[c]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

The absorption, fluorescence, and excitation spectra of two cation-anionic dyes with simple structures, which have the identical anions and variable cations, were studied in weakly polar and nonpolar solvents as well as in binary mixtures of solvents with different polarity. Under these conditions heterogeneous fluorescent aggregates were found at 20 °C. The structure of the cation has a significant influence on the formation and properties of the aggregates of cation-anionic polymethine dyes.

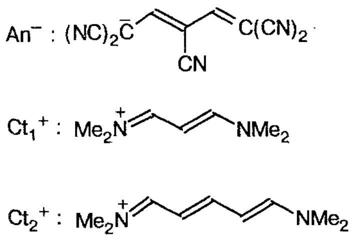
Key words: fluorescence and absorption spectra, cation-anionic polymethine dyes, aggregates, ion pairs.

The processes of molecular association of polymethine dyes (PD) have been studied in water[1] and organic solvents.[2] In most cases the associated molecules do not possess the property of luminescence at room temperature. In spite of a great deal of investigation, many problems concerning the processes of the molecular association of PD remain to be solved due to their complexity and diversity. The association of PD has been studied mainly in dyes with a single chromophore because they are widely used as photosensitizers.[3]

Until recently, mainly the association of identical molecules of dyes (homogeneous aggregates) has been investigated. However, aggregates may also be formed from different dye molecules (heterogeneous aggregates), which results in a difference between the electron spectrum of the mixture and the sum of the spectra of its components.[4,5] The formation of heterogeneous aggregates has been poorly studied. The analysis of the conditions under which the formed aggregates possess the property of luminescence is of considerable scientific and practical interest due to the use of mixtures of different dyes as operating media in dye lasers,[6] and emission transformers.[7] It is of interest to elucidate the relationship between the luminescent capacities of substances and their structures. Detailed reviews devoted to the association of dye molecules have been presented in articles[6,9].Recently, the fluorescent aggregates of some cation-anionic PD containing cation and anion dyes (heterogeneous aggregates) were found and studied.[10] In this study two cation-anionic PD with simple structures (without terminal heterocycles), which have a common anion but variable cations and differ in the length of the polymethine chain, are investigated.

Experimental

Two cation-anionic PD (**1** and **2**, respectively) having a common anion (An^-) and two variable cations (Ct_1^+ and Ct_2^+) were studied.



"Pure" grade acetonitrile, chloroform, carbon tetrachloride, hexane, "analytical" grade toluene, dioxane (scintillation grade) and their mixtures were used as solvents. Acetonitrile was purified by consecutive refluxing over NaH, P_2O_5, and CaH_2 followed by distillation. Chloroform was allowed to pass through a column packed with Al_2O_3 to remove the traces of acid. Toluene was purified by distillation over sodium. Fluorescence spectra were recorded with an Aminco-Bowman instrument equipped with an R136 photomultiplier (spectra were not corrected). Absorption spectra were recorded with a Specord

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UV-VIS instrument. The absorption spectra of dye solutions in a cell with a 1 cm optical path (dye concentration was usually (1—4) 10^{-5} mole L^{-1}) are given.

All measurements were carried out at 20 ± 1 °C.

Results and Discussion

As has been shown previously[11,12] the fluorescence spectral characteristics of cation-anionic PD in polar solvents (in acetonitrile, in particular) are close to the corresponding parameters of their constituent cations and anions because they are almost completely dissociated in these media. Significant spectral differences are observed in weakly polar and nonpolar solvents. For the latter additional bands appear in the absorption and fluorescence spectra of these dyes. This may be caused both by the formation of ion pairs (interaction of the chromophores in the ion pairs[11]), and by the formation more complex associates, dye aggregates.[10]

Let us consider the absorption and fluorescence spectra of PD (Fig. 1). The absorption bands of its cation and anion differ by ~100 nm (in acetonitrile λ_{max}^{abs} 311 and 417 nm, respectively). Therefore, the interaction of the cation and anion chromophores in the ion pairs should be negligible.[11] On passing from polar acetonitrile (dielectric constant ε 37) to weakly polar chloroform (ε 4.7), in which the formation of ion pairs of the anion and cation becomes significant, no new bands appear in either the absorption or the fluorescence spectra. Only the long-wave shift of the bands due to the higher refractive index of chloroform in comparison with acetonitrile is observed. This points to the absence of aggregation of PD **1** under these conditions. However, in a solvent of even lower polarity, dioxane (ε 2.2), a new luminescence band with λ_{max}^{fl} 568 nm (see Fig. 1, *b*) appears. This band can be attributed to the fluorescence of aggregates.

The formation of PD **1** aggregates is also observed when the dye is dissolved in binary mixtures of solvents. Figure 2 demonstrates the changes in the absorption and fluorescence spectra of PD **1** taking place in chloroform — hexane solvent mixtures gradually passing from chloroform to hexane. In pure hexane the aggregates are absent, but when the content of hexane is 50 % or higher the intensity of the initial bands of the dye decreases, and new absorption bands with λ_{max}^{abs} 380 nm and fluorescence bands with λ_{max}^{fl} 575 nm caused by the formation of aggregates emerge.

It should be noted that the addition of acetonitrile (50%) to the aggregates containing dye solution, which leads to their disappearance, was used to identify the bands of the aggregates. Moreover, as dye concentration decreases the relative intensity of the aggregate bands decreases.

Unlike PD **1**, PD **2** is characterized by absorption bands of the cation and anion that almost coincide, hence its spectrum in acetonitrile has a single absorption band with λ_{max}^{abs} 413 nm (see Fig. 3, *a*). In ion pairs of this dye in weakly polar solvents the interaction of the chromophores of the cation and anion is observed, which should result in the appearance of an additional short-wave absorption band[11] inactive in fluorescence excita-

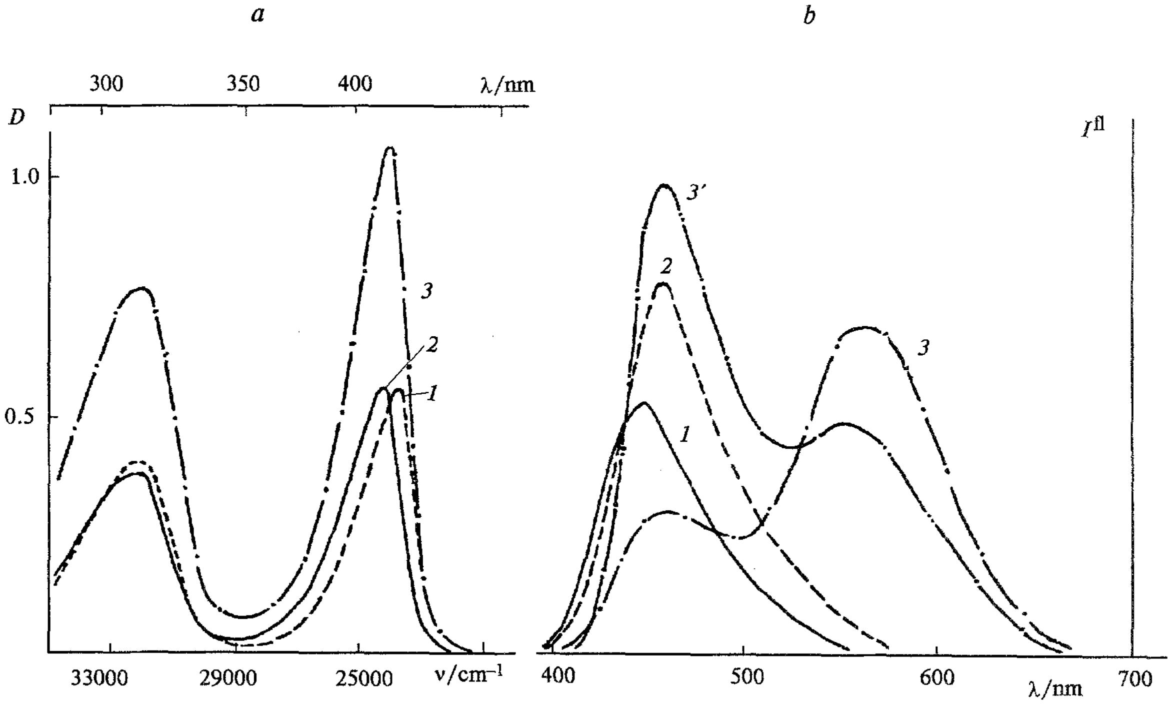


Fig. 1. Absorption (*a*) and fluorescence (*b*) spectra of PD **1** in acetonitrile (*1*), chloroform (*2*) and dioxane (*3, 3'*); (*3'* is more dilute solution); *b*: λ^{ex} 400 nm.

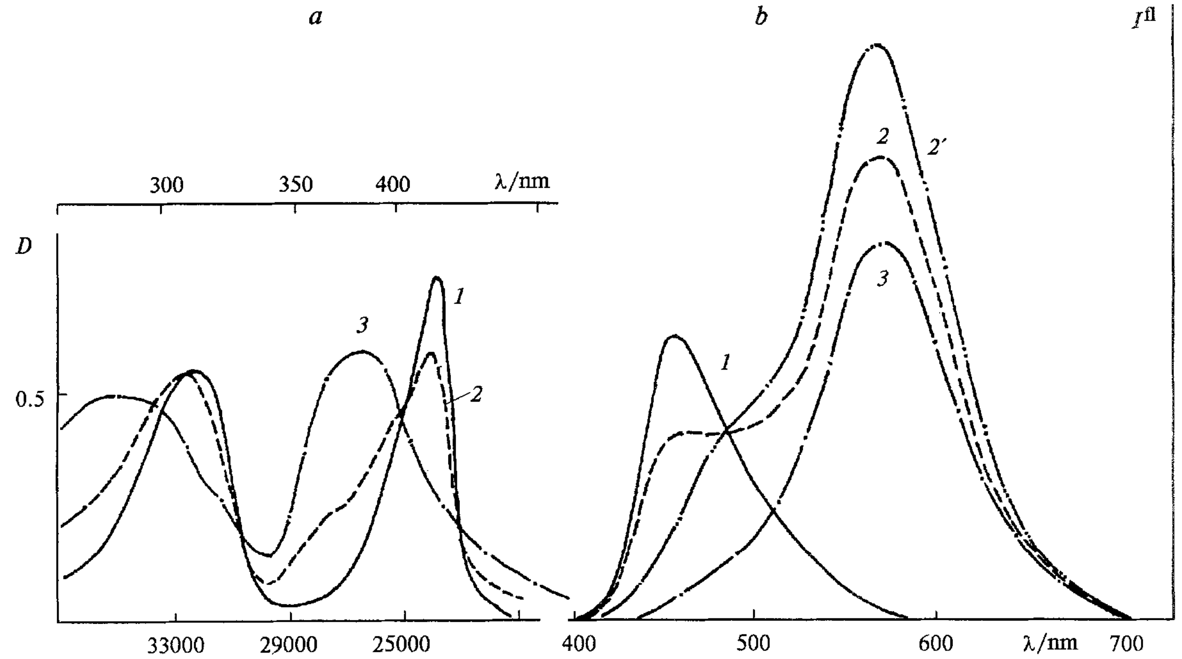


Fig. 2. Absorption (*a*) and fluorescence (*b*) spectra of PD **1** in chloroform — hexane solvent mixtures: *1*, 100%, *2*, *2′*, 50 %, *3*, 20 % of chloroform; *b*: λ^{ex} 400 (*1*), 380 (*2*, *3*) and 360 nm (*2′*).

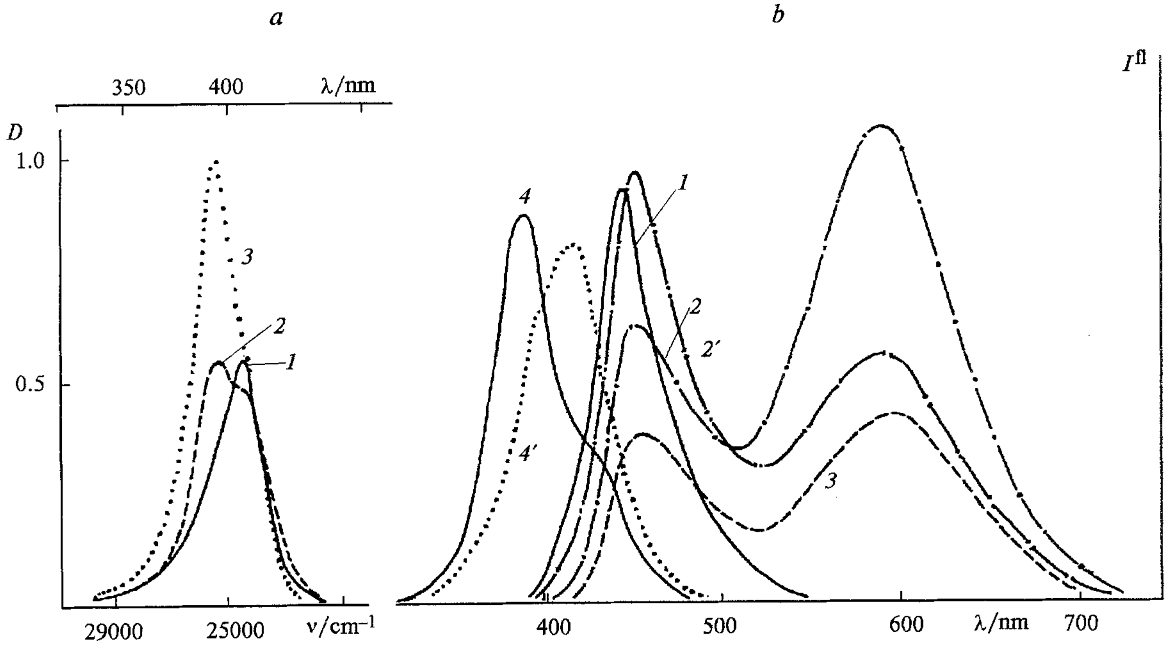


Fig. 3. Absorption (*a*), fluorescence, and excitation (*b*) spectra of PD **2** in acetonitrile (*1*), chloroform (*2*, *2′*, *4*,*4′* (*4*, *4′*, excitation spectra), and toluene (*3*); *b*: λ^{ex} 410 (*1*, *2′*) and 390 nm (*2*, *3*), λ^{fl} 600 (*4*) and 460 nm (*4′*).

tion.[12] For PD **2** the appearance of a short-wave band with λ_{max}^{abs} 398 nm actually takes place when passing from acetonitrile to chloroform. However, the excitation of this band leads to the emergence of a long-wave fluorescence band with λ_{max}^{fl} 595 nm. In a solvent of even lower polarity, toluene, the relative intensities of the new absorption and fluorescence bands increase, while the intensities of the initial bands of the dye decrease (see Fig. 3). The excitation spectrum of the new fluorescence band corresponds to the short-wave absorption band (see Fig. 3). Tests demonstrated that the new bands were caused by the formation of fluorescent aggregates of PD

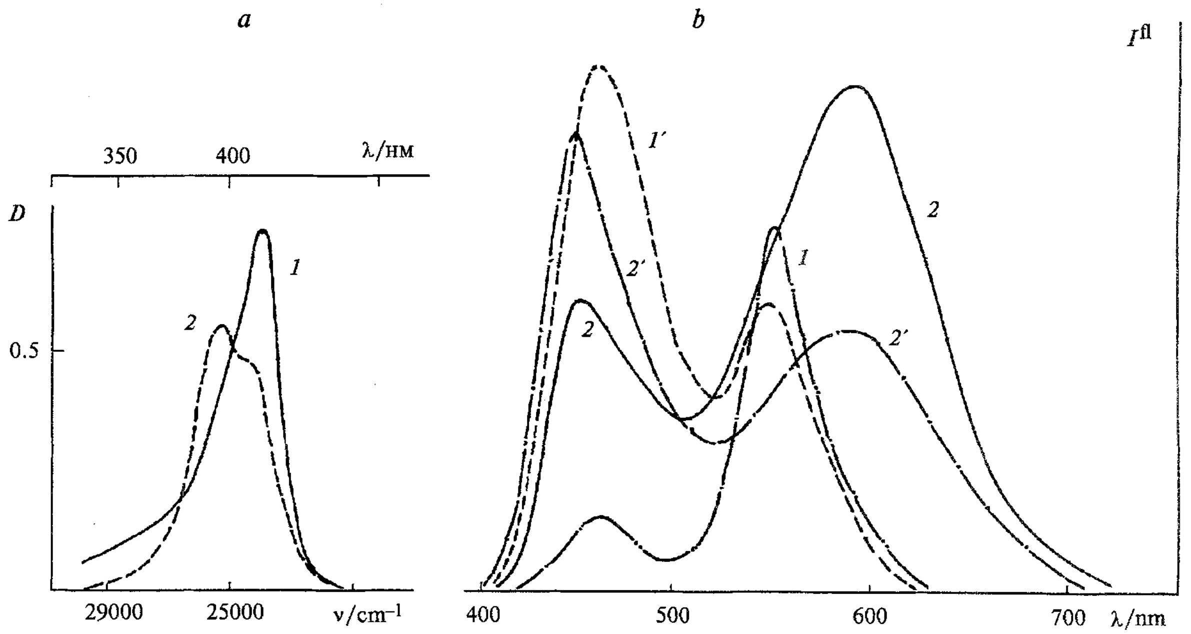
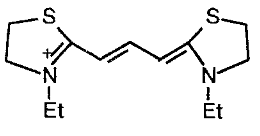


Fig. 4. Absorption (*a*) and fluorescence (*b*) spectra of PD **2** (*1, 1'*) and PD **3** (*2, 2'*) in chloroform; *b*: λ^{ex} 410 (*2'*), 400 (*1'*), 390 (*2*) and 360 nm (*1*).

2. In this case the short-wave absorption band caused by the interaction of the chromophores in the ion pairs is likely to be superimposed on the absorption band of the aggregates and to mask it.

Notice that, unlike ordinary PD, cation-anionic PD associates form heterogeneous aggregates containing both cationic (Ct^+) and anionic (An^-) dyes together. The association process of such PD in solvents with decreasing polarity may be presented as follows: at first Ct^+An^- ion pairs are formed, as solvent polarity decreases, they approach each other and unite into dimers, trimers, and more complex associates according to the scheme: $Ct^+An^-...Ct^+An^-...Ct^+An^-...$[13]

The influence of the nature of the cation on the ability of PD to associate and the properties of the aggregates may be elucidated by comparing PD **1** and **2** with similar PD investigated earlier,[10] which have a common anion An^-, but different cations: the simple cation $Me_2\,NH_2^+$ (anionic PD **3**) and the bulky cation-dye:



(cation-anionic PD **4**).

As has been shown,[10] PD **3** and **4** like PD **2** form fluorescent aggregates in chloroform. In this case the fluorescence band of the PD **3** aggregates is shifted to the short-wave region and is considerably narrower than the fluorescence bands of the PD **2** and **4** aggregates, which have much the same width and position in the spectrum (see Fig. 4 and Ref. 10). The absorption bands of PD **3** and **4** aggregates like PD **2** aggregates fall in the short-wave region with respect to the absorption spectra of the initial dyes. However, PD **1** does not form aggregates in chloroform because its cation has a shorter polymethine chain than those of PD **2** and **4**. Therefore, by comparing PD **2** with **4** it may be concluded that the introduction of terminal heterocycles into the structure of the cation Ct_2^+ has no substantial effect on the fluorescence spectra of the aggregates formed by them. At the same time the length of the cation polymethine chain is of great significance: PD **1** does not form any aggregates in chloroform. On the other hand, an even simple dye, anionic PD **3**, forms such aggregates (their narrower fluorescence band seems to indicate that the aggregates have a more ordered structure).

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