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4-(4-Dimethylaminostyryl)pyridinium derivative: a solvent viscosity- and polarity-sensitive fluorescent sensor*

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Trans-4-(*p*-N,N-dimethylaminostyryl)-N-vinylbenzylpyridinium chloride (1) is a newly synthesised multichromophore chemosensor. This molecule displays strong intramolecular charge transfer properties. It fluorescences in a very favourable region (480–650 nm in polar and viscous solutions) for its use as a sensing system. Steady-state and time-resolved fluorescence spectroscopy have been used to characterize photophysical properties in viscous and non-viscous polar solutions. We investigated the influence of solvent viscosity on the rate constants of radiative and non-radiative processes of deactivation of (1) in aqueous solutions.

Key words: *multichromofore chemosensor; polarity sensitive fluorescence; reorientation processes*

1. Introduction

Multichromophore compounds exhibiting intramolecular charge transfer (ICT) and twisted intramolecular charge transfer (TICT) properties show ICT fluorescence bands that depend on the physical and chemical properties of the medium. This environmentally sensitive fluorescence, by virtue of varying fluorescence responses to solvent media, provides a wealth of information on the molecular properties of microenvironments. In particular, the dependence of TICT fluorescence on viscosity of the environment has been widely reported, and is thought to occur by a time-dependent

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intramolecular reorientation process [1–5]. The applications of environmentally sensitive fluorophores are limited by their fluorescence wavelength ranges. Although a number of fluorophores are used, only few of them have absorption and fluorescence spectra in the visible range. Among them dimethylaminostyrylpyridinium derivatives are important as they are easily composed into a polymer matrix. The dynamics of reorientation relaxation of molecules in solution with high friction between the rotating molecule and solvent, as it occurs for 4-(4-dimethylaminostyryl)pyridine (DMASP) derivatives, can be described by the Debye–Stokes–Einstein (DSE) hydrodynamic model. The reorientation relaxation time of the solvent molecules τ_{or} depends on the viscosity and on fluorescence quantum yield Φ_F, as shown by the following equations [1–3]:

$$\tau_{or} = C(\eta/T) \tag{1}$$

$$\tau_{or} = \tau \frac{\Phi_F}{\Phi_0 - \Phi_F} \tag{2}$$

where η is the shear viscosity of the solvent, T is the absolute temperature, C is the geometry-dependent rotational friction coefficient (which itself is dependent on temperature and viscosity [6]), τ is the lifetime of fluorescence of the dye, and Φ_0 is the fluorescence quantum yield when internal rotation of the molecule has ceased (at infinite η). If $\Phi_F << \Phi_0$ ($\Phi_0 = 0.35$) for the dye in a polymer matrix [2, 5], the above equations simplify to:

$$\Phi_F = \Phi_0 (C/\tau)(\eta/T) \tag{3}$$

This relationship has been proven for many compounds exhibiting ICT properties, including *p*-(dimethylamino)benzonitrile [1], substituted stilbenes [4], *p*-dialkylaminobenzylidenemalononitriles [2] and 4-(*p*-dimethylaminostyryl)pyridine derivatives [5, 7]. Increase of the viscosity of the environment surrounding of these fluorophores, suppresses the non-radiative transitions induced by intramolecular reorientation and diffusional collisions with the solvent molecules, and thus enhances the radiative processes [4, 5, 7].

Sensory systems based on DMASP exhibit environmentally sensitive photoinduced electron transfer and conformational changes in the meaning of viscosity and polarity interactions [3, 5, 7–9]. Recently, DMASP derivatives were reported to be sensitive to viscosity and temperature in aqueous solutions [5, 9]. These molecules are charged fluorophores with ICT fluorescence in the visible regions, about 600 nm that can be observed with excitation at 360 and 469 nm. Although the intensity of ICT emissions obtained by excitation at both 469 and 360 nm was affected by the viscosity of the local microenvironment, the emission obtained by excitation at 469 nm exhibited the greatest enhancement with viscosity, while that obtained by excitation at 360 nm was much less sensitive to the changes in viscosity. In this paper, we present new data on the viscosity dependence of the reorientational dynamics of (1) in viscous aqueous glycerol and non-viscous methanol solvents. The goal of this study is to characterize the radiative and non-radiative deactivation processes for better understanding the solute–solvent interactions that influence the fluorescence of the sensing system.

2. Experimental

2.1. Materials

4-(4-Dimethylaminostyryl)pyridine (95%) and 4-vinylbenzyl chloride (90% *p*-vinylbenzyl chloride), acetonitrile, methylene chloride and carbon tetrachloride were purchased from the Aldrich Chemicals Co., and used without further purification. Methanol (99,9% HPLC grade) and glycerol (99% GC) were purchased from Sigma Chemicals Co., and used without purification. Aqueous solutions were prepared using double distilled deionised water.

2.2. Synthesis of *trans*-4-(*p*-N,N-dimethylaminostyryl) -N-vinylbenzylpyridinium chloride

Acetonitrile (10 cm^3) was added to a round bottom flask containing (0.246 g, 1.1 mmol) DMASP equipped with a magnetic stirrer, reflux condenser topped with a nitrogen inlet and a heating mantle. When DMASP was completely dissolved (for minimum 24 hours), it was stirred under nitrogen at the temperature of 60 °C, 4-vinylbenzyl chloride (0.256 g, 1.68 mmol) was added dropwise for over 15 min to give an orange reaction mixture. After gentle refluxing for ~48 h under nitrogen any remaining undissolved material was filtered off, leaving a clear, deep red mother liquor which was rotoevaporated to dryness. The product was recrystallized from methylene chloride and carbon tetrachloride and dried under vacuum (20 mm Hg) at 35 °C overnight. Yield of the product – dark red crystals – was 0.378 g (78.5%).

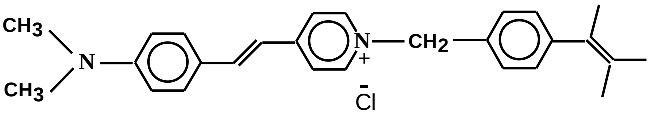


Fig. 1. Molecular structure of *trans*-4-(*p*-N,N-dimethylaminostyryl) -N-vinylbenzylpyridinium chloride (1)

The ^1H NMR spectra were recorded using Bruker Avance DPX 250:

^{1}H NMR ($CDCl_3$) δ 3.09 ppm (s. 6H, CH_3), 5.26 ppm (d. 1H, H_b), 5.72 ppm (d. 0.3H, *para* H_a), 5.79 ppm (d. 0.7H, *meta* H'_a), 6.04 ppm (s. 2H, CH_2), 6.66 ppm (m. 1H, H'), 6.69 ppm (d. 2H, H), 6.77 ppm (d. 1H, H), 7.26 ppm (t. 0.7H, *meta* H'_a), 7.35 ppm (d. 1.3H, *meta* H and *para* H), 7.53 ppm (d. 1H, H), 7.56 ppm (d. 0.6H, *para* H), 7.58 ppm (s. 0.7H, *meta* H), 7.75 ppm (d. 2H, H), 9.17 ppm (d. 2H, H). The structure of the molecule is schematically shown in Fig. 1.

2.3. Viscometry

The viscosities of the solvents were determined using capillary Ubbelohde dilution type viscometers which were submerged in a bath at the temperature of 25±0.1 °C. Solutions of various viscosities were prepared from water and glycerol mixtures and the average kinematic viscosity was taken as the mean of four measurements. Then the average kinematic viscosity was converted to intrinsic viscosity and corrected for density. The viscosities of highly concentrated aqueous glycerol solutions were obtained from published tables [10]. Low-viscosity binary solutions were prepared from water and methanol mixtures.

2.4. Spectroscopy

Absorption spectra were taken using a UV-VIS Varian Cary spectrometer and fluorescence spectra using a Perkin Elmer LS 50 spectrofluorimeter. Time-correlated single photon counting system (Edinburgh Analytical Instruments Co.) was used in fluorescence lifetime measurements. The fluorescence decays were analysed by a last squares reconvolution procedure using the software package provided by Edinburgh Instruments. 10 nm excitation and emission slits were used when both steady-state and time-dependent fluorescence spectra were recorded.

To avoid aggregation and self-quenching processes, the dye concentration of 10^{-5} M was used. The cuvette holder was heated with the accuracy of ± 0.1 deg. Fluorescence quantum yields (Φ_F) were determined at 25 °C relative to the quantum yield of rhodamine B in ethanol ($\Phi = 0.69$; excitation at 366 nm) as a standard (Φ_{st}), using the following equation [11]:

$$\Phi_F = \Phi_{st} \frac{I_F}{I_{st}} \frac{A_{st}}{A_F} \tag{4}$$

where I_F and I_{st} are the fluorescence emission peak area of the dye solution and the standard solution, respectively; A_{st} and A_F are the absorbances of the standard solution and the dye solution, respectively.

3. Results and discussion

Figure 2a shows UV-Vis absorption spectra of (1) in water and in viscous solutions of mixture of glycerol with water. The absorption band appears as a typical ICT broad transition in the 350–550 nm region. The single broad absorption band of (1) exhibited a $\lambda_{\max}$ at 459 nm, very similar to that obtained for other DMASP derivatives [5, 8]. There is a bathochromic shift of the $\lambda_{\max}$ when (1) is in the aqueous glycerol solutions (Fig. 2a) up to 494 nm in 99% glycerol, and in aqueous methanol (Fig. 2b) up to 489 nm for 100% methanol. Excitation of (1) at 469 nm resulted in a broad structureless emission band with a maximum at 600 nm in water, as shown in Fig. 3a.

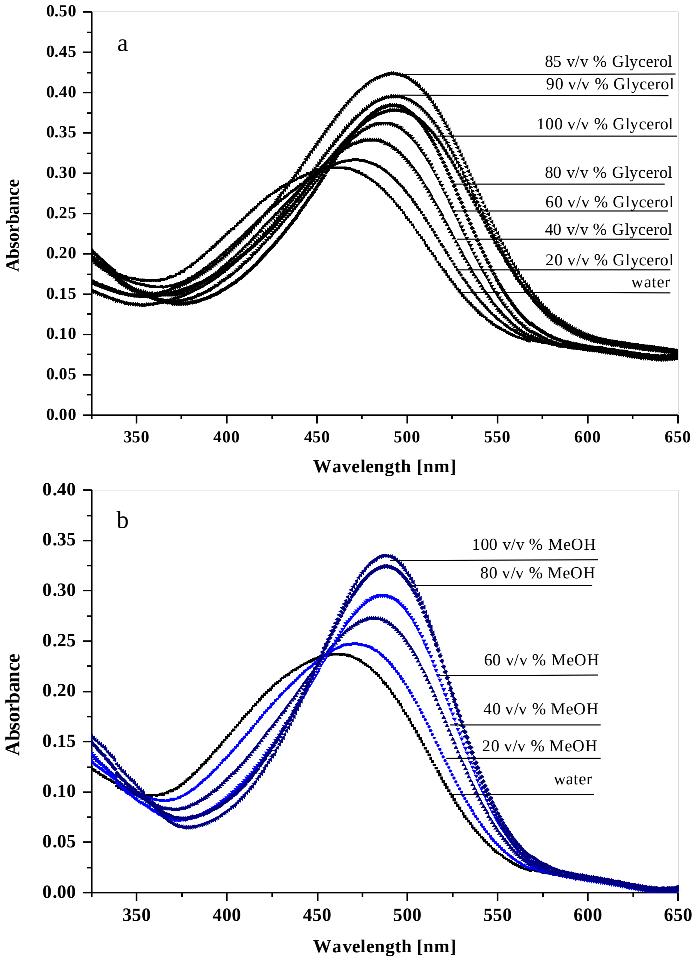


Fig. 2. Absorption spectra of (1) (10^{-5} M) in binary aqueous solvents:
a) glycerol–water, b) methanol–water

The band slightly moves to shorter wavelengths with an increase of glycerol concentration in the mixed solvent but the intensity increases dramatically when the concentration of glycerol as well as its viscosity increase. Similarly, when (1) was in mixed methanol and water solvent shown in Fig. 3b, the shift of maximum wavelength was about 5 nm. Excitation of (1) at 360 nm resulted in a broad structured emission spectrum that could be decomposed by curve-fitting analysis ($r > 0.995$, standard error ±10%) into Gaussian emission peaks. The deconvoluted peak with a maximum at 600 nm appeared to be similar to the broad emission band obtained by excitation at 469 nm as was previously presented for other DMASP derivative, *trans* -4-(*p*-N,N-dimethylaminostyryl)-N-phenethylpyridinium bromide [5]. The quantum yields of the ICT of longer wavelengths [5] were calculated and shown in Table 1.

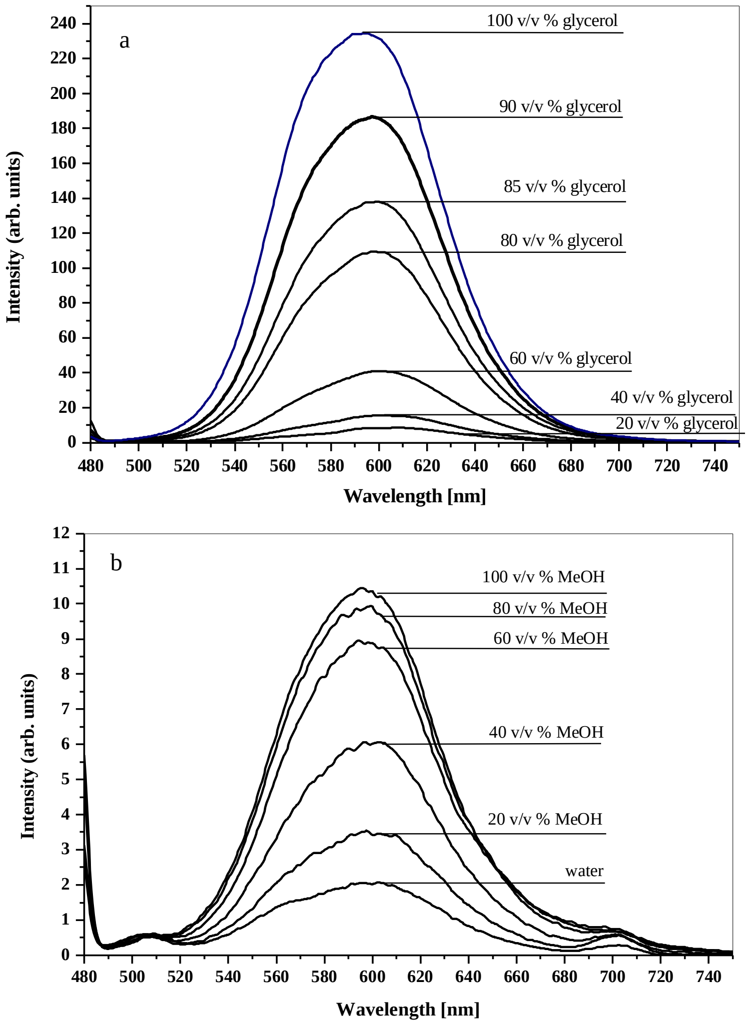


Fig. 3. Fluorescence spectra of (1) (10^{-5} M) in binary aqueous solvents when excited at 469 nm: a) glycerol–water, b) methanol–water

The intensity of this ICT fluorescence was comparable to that obtained by excitation at 469 nm and it corresponds to the data obtained for DMASP derivative [5]. The ICT fluorescence by excitation at 360 nm was observed for (1) in binary water –methanol solvents and is at about 500 nm, the emission at 600 nm is negligible. Presumably the structure of the molecule is slightly different. For the aqueous vbDMASP the Stockes shift is about 140 nm, and shifts to 100 nm for pure glycerol while for the methanol–water binary solvent of vbDMASP it shifts to 108 nm.

Table 1. Fluorescence quantum yield for (1) in viscous and non-viscous aqueous solvents

Component's concentration (v/v %)	Viscous solutions Glycerol–water			Non-viscous solutions Methanol–water		
	Viscosity (T = 298 K) cP	Quantum yield$\times10^2$		Viscosity (T = 298 K) cP	Quantum yield$\times10^2$	
		Exc. 469 nm	Exc. 360 nm		Exc. 469 nm	Exc. 360 nm
0 (pure H_2O)	0.89	0.111	0.137	0.89	0.109	0.137
20	1.54	0.205	0.290	1.53	0.221	0.182
40	3.18	0.379	0.371	1.67	0.282	0.245
60	8.82	1.001	0.582	1.48	0.349	0.310
80	45.90	2.936	1.110	1.07	0.399	0.362
85	96.00	3.764	1.593	–	–	–
90	267.00	5.135	1.835	–	–	–
100 (glycerol or methanol)	934.00	7.300	2.241	0.54	0.355	0.317

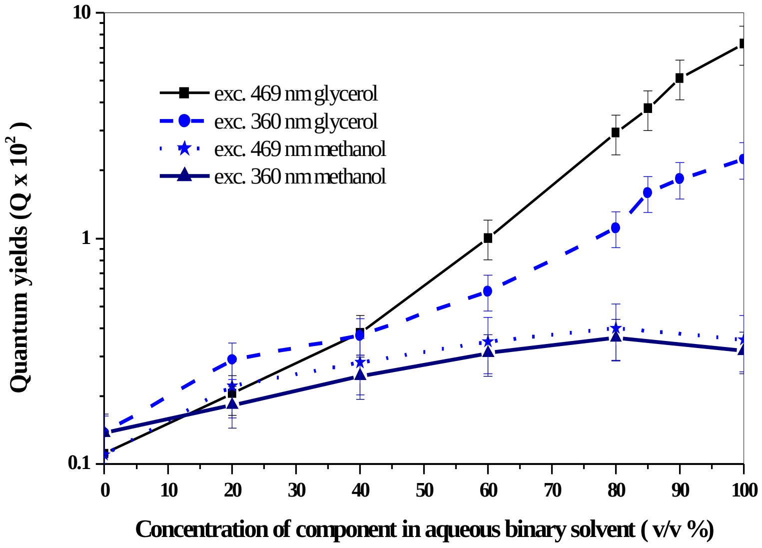


Fig. 4. Fluorescence quantum yield of (1) (10^{-5} M) in binary aqueous solvents when excited at 469 and 360 nm. The experimental values are means of four measurements

Figure 4 shows the quantum yield of fluorescence of (1) dependent on the concentration of binary solvent. The fluorescence quantum yield for (1) in aqueous glycerol increases with the concentration of glycerol but it slightly changes for that in the aqueous methanol binary solvent. The results suggest that the quantum yield of the molecule is strongly affected by the reorientation relaxation processes in agreement with Eq. (1).

Table 2. Fluorescence lifetime τ, ns for (1) in viscous and non-viscous aqueous solvents

Component's concentration (v/v %)	Viscous solutions Glycerol–water		Non-viscous solutions Methanol–water	
	Exc. 360 nm	Exc. 469 nm	Exc. 360 nm	Exc. 469 nm
0 (pure H$_2$0)	0.188*	0.115*	0.188*	0.115*
20	0.223*	0.141*	0.220*	0.127*
40	0.276*	0.182*	0.265*	0.144*
60	0.355±0.07	0.261±0.06	0.332*	0.161*
80	0.546±0.03	0.424±0.05	0.452±0.14	0.193±0.04
85	0.628±0.16	0.539±0.04	–	–
90	0.641±0.15	0.5895±0.04	–	–
100 (glycerol or methanol)	0.98	0.744*	0.542±0.11	0.240±0.06

*The data were obtained by extrapolation of linear dependence of 1/τ vs. of binary solvent components' concentration (v/v %).

We measured the lifetimes of fluorescence of (1) when excited at 469 and 360 nm in viscous and non-viscous polar solutions. The data are gathered in Table 2.

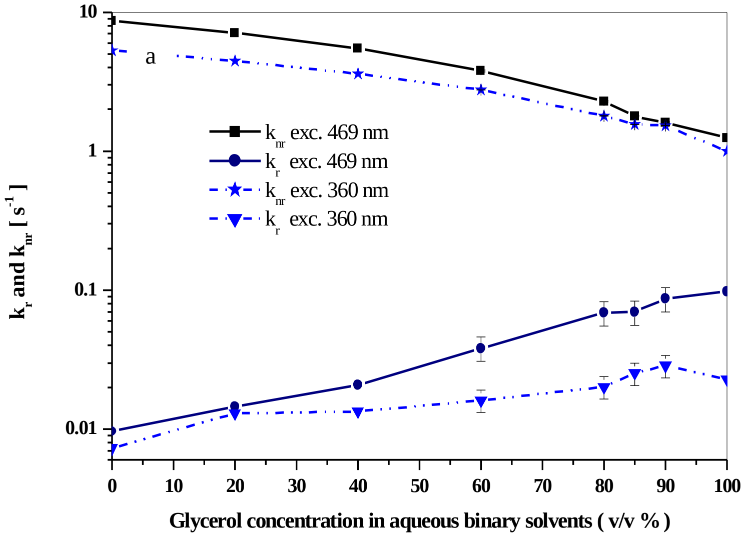
The lifetime increases with the concentration of the viscous component in the binary solvent and much less for the non-viscous binary solvent, the lifetime for (1) in glycerol-based solvent is three times as high as for methanol-based solvent, if excitation was at 469 nm. When solution of (1) was excited at 360 nm, lesser increase of the fluorescence lifetime is observed (Table 2). This indicates that the lifetime of fluorescence is affected by viscosity as well as by electrostatic interactions but the effect of viscosity is much higher.

The basic photophysical equation which correlates the quantum yield and lifetime of fluorescence of the molecule with rate constants of radiative and non-radiative processes can be defined as follows [5]:

$$k_r = \frac{\Phi_F}{\tau_F}; \qquad k_{nr} = \frac{1-\Phi_F}{\tau_F} \tag{5}$$

where: Φ_F – quantum yield at a given concentration of the solvent and wavelength, τ_F – fluorescence lifetime at a given concentration of the solvent.

Figures 5a, b show the rate constants of radiative and non-radiative processes of (1) in the binary aqueous solvent systems, viscous and non-viscous, respectively. The increase of the rate constants of radiative processes due to (1) in viscous glycerol –water solutions with an increase of the glycerol concentration in the mixture is accompanied by a decrease of the rate constants of non-radiative processes.



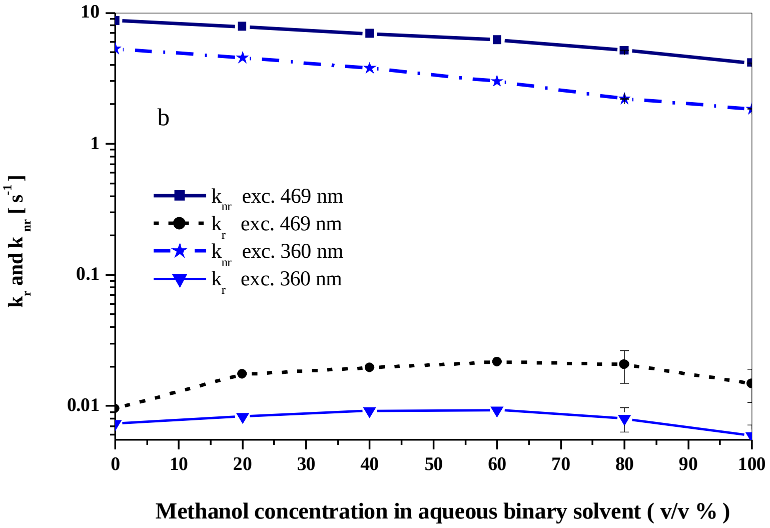


Fig. 5. Rate constants of radiative and non-radiative process for 1 in binary solvents vs. solvent concentration when excited at 469 and 360 nm. The experimental values are means of four measurements; a) glycerol–water, b) methanol–water

In opposite, for non-viscous methanol–water binary solvent the rate constants of radiative deactivation slightly increase with addition of methanol (10 v/v %) and almost do not change with the concentration of methanol in the binary solvent. In opposite (Fig. 5b), for non-viscous methanol–water binary solvent the rate constants almost do not change with the concentration of methanol in the binary solvent.

Conclusions

The vbDMASP probe molecules exhibit an intense absorption band in the visible region. The long-wavelength $S_0 \rightarrow S_1$ absorption band was observed to move to generally lower energies with the increasing concentration of glycerol in the mixture with water, which results in increasing viscosity. Fluorescence emission spectra ($S_1 \rightarrow S_0$) exhibited the same sensitivity to solvent viscosity demonstrating the role of non-radiative deactivation of the excited state of the dye. The decrease of the rate constant of non-radiative deactivation processes with the increase of glycerol concentration in the aqueous solution is accompanied by an increase of radiative deactivations. The long-wavelength fluorescence emission of vbDMASP observed in the glycerol–water binary solvent is undoubtedly due to an intramolecular $\pi^* \rightarrow \pi$ charge-transfer transition. A question can be raised, however, as to whether the conformation of the multichromophore compound and the fluorescence observed in viscous solvents will change when the compound is incorporated to polymer matrix. We have no answer to this question yet but no change of the absorption and fluorescence spectra, in the meaning of maximum wavelength and its CT character, has been observed when the molecule was covalently incorporated in the polymer matrix. The vbDMASP has the possibility to be easily incorporated in the polymer matrix.

Acknowledgements

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