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Solvent effects on the photophysical properties of poly[1,4-dihydroxyanthraquinoneimine-1,3-bis(phenylene-ester-methylene)tetramethyldisiloxane]

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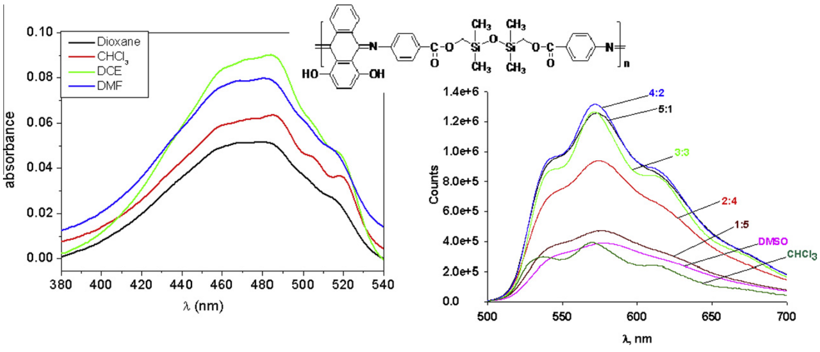
HIGHLIGHTS

- Solvatochromic behavior of a polyquinoneimine is analyzed.
- Solvent–solute interactions are described by their effect on spectral behavior.
- Spectral shifts were correlated with solvent parameters.
- Photoluminescence quantum yield has been evaluated in different solvents.

GRAPHICAL ABSTRACT



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ABSTRACT

Absorption and fluorescence spectra of a polyquinoneimine, PQI, built on 1,4-dihydroxyanthraquinone and a siloxane diamine, 1,3-bis(amino-phenylene-ester-methylene)tetramethyldisiloxane, have been investigated in solvents of different polarities. The effect of solvents on the spectral properties was investigated using Lippert–Mataga and Bakhshiev polarity functions and Catalán's multiple linear regression approach. Absorption and fluorescence spectra in studied solvents exhibit hypsochromic and bathochromic shifts, respectively. The polarity of the solvent was the main parameter which changes the spectral properties of PQI. Also, the binary mixtures of chloroform with methanol and dimethyl sulfoxide were used to analyze the intermolecular interactions and preferential solvation. The preferential solvation parameters (local mole fraction (X_2^L), excess function (δ_{s2}) and preferential solvation constant (K_{PS})) were calculated from spectral data and discussed as a function of cosolvent content. The values of quantum yield, decreased linearly with increasing solvent polarity (for non-polar and polar solvents).

Introduction

Anthraquinone and its derivatives bearing hydroxy and amino moieties are of remarkable importance in pharmacological, biochemical and dye industries [1,2]. They have been described as important compounds for decades and they are used for the coloration of cotton and cellulose fibers as well as for synthetic materials such as polyamides. Anthraquinone dyes have the advantage that they are resistant of degradation process due to their aromatic structure [3–6].

Several properties of dyes in solutions depend on the nature of their solvent environment. The solvent-dependent spectral shifts may arise from either non-specific interactions (polar and van

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der Waals interactions) or specific solute–solvent interactions (hydrogen bonding, donor–acceptor interactions) [7–11]. Knowledge of the contributions of both types of solute–solvent interactions is significant in the analysis of solvent effects. The solute–solvent polarizability as well as solute–solvent polarity plays a particular role in the solute spectral properties. The solvent effect is closely related to the nature and degree of intermolecular solute–solvent interactions.

Thus, the systematic analysis on solvent effect provides important information in investigating the excited state behavior of the molecule. A change in solvent is accompanied by a change in polarity, dielectric constant, viscosity or change in polarizability of the surrounding environment. Therefore, a change in solvent can influence differently the ground and excited states due to the difference in the solvation energies which are determined by the electron distribution in these states, leading to various shifts in the electronic absorption spectra or in emission spectra of the solute. In this case a positive or negative solvatochromism can be produced giving thus qualitative or quantitative information about the energetics of the molecule solvation. The study of excited state properties helps us not only in the design of new compounds but also for a better performance in analysis of potential applications of some solvent-dependent molecules in order to obtain new data about the molecular environment in cells or macromolecules [12]. Excitation of a molecule gives rise to redistribution of charges and electron densities leading to conformational changes in the excited state [13–15].

Interactions in mixed solvent systems are more complicated than those occurring in pure solvents due to the interference of solvent–solvent and solute solvent interactions. For this reason, the molecules of solute can determine a change in the composition of cybotactic region in comparison to the bulk composition [16].

Hereby we describe the absorption and emission characteristics of a new siloxane anthraquinone derivative (Fig. 1) in different solvents in order to estimate which type of solvent interactions determines significant shifts on the position of the spectral bands. The particularity of the approached structure consists in its amphiphile nature conferred by the co-existence of highly hydrophobic tetramethyldisiloxane moiety alternating with polar ester-hydroxyazomethine one within the chain. Comparatively, the influence of solute–solvent and solvent–solvent interactions on the preferential solvation behavior was analyzed in binary mixtures. The solvent influence on the quantum yield was also discussed.

Experimental

Synthesis of poly[1,4-dihydroxyanthraquinoneimine-1,3-bis(imino-phenylene-ester-methylene)tetramethyldisiloxane], PQI

In a 100 mL round bottom flask equipped with magnetic stirrer, nitrogen inlet and reflux condenser protected with $CaCl_2$ tube, 1,3-bis(amino-phenylene-ester-methylene)tetramethyldisiloxane (0.432 g, 1 mmol) prepared in our laboratory [17], 1,4-dihydroxy-anthraquinone (0.240 g, 1 mmol) and dry dimethylformamide (DMF) (30 mL) were introduced. The mixture was refluxed under stirring for 48 h, and then the resulting product was precipitated in water (100 mL) and was extracted with chloroform (3×50 mL). The formed polymer was isolated by the chloroform removing, washed with water and petroleum ether and dried in vacuum at 50 °C. A brown crystalline powder, soluble in polar aprotic solvents like DMF and dimethyl sulfoxide (DMSO) and non-polar solvents like $CHCl_3$, was obtained. The formation of polyquinoneimine was confirmed through FTIR and ^1H NMR spectra.

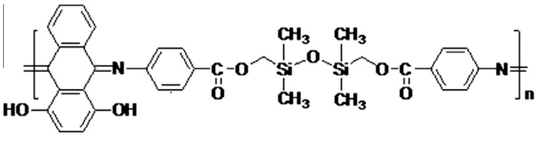

Fig. 1. Chemical structure of the polyquinoneimine, PQI.

IR spectrum (KBr pellet), cm^{-1}: 3468m, 3418m, 3364m, 3235w, 2959w, 2907w, 1697vs, 1674s, 1630vs, 1593vs, 1516s, 1454s, 1412m, 1393m, 1358s, 1313vs, 1300vs, 1256vs, 1227s, 1215s, 1171s, 1150s, 1115s, 1069s, 1049s, 1028s, 964m, 874m, 843s, 795s, 772s, 725m, 698m, 660w, 636w, 608m, 579m, 548w, 498m, 455w, 422w, 393vw.

^1H NMR ($CDCl_3$, 400.13 MHz, δ, ppm): 1H RMN ($CDCl_3$, 400 MHz, ppm: 8.36–8.33 (m, Ar–H), 7.84–7.81 (m, Ar–H), 7.30 (s, Ar–H), 6.63–6.06 (m, Ar–H), 3.9 (s, $-CH_2-$), 0.21 (s, $Si-CH_3$).

Method

The electronic absorption spectra were recorded with a Shimadzu 3600 spectrophotometer using pair quartz cells of 10 mm optical length. Fluorescence spectra were measured using a FLS 980 fluorospectrometer from Edinburgh Instruments or Perkin Elmer LS55 luminescence spectrometer in 10 mm quartz cells. The excitation wavelength was set in the absorption band maximum of the sample. The fluorescence quantum yield was determined using a FLS 980 spectrometer with integrated sphere in different solvents, at room temperature. The measurements were performed at an absorbance value of ~0.01 in a 10 mm path cell in order to avoid self-absorption effect. Binary mixtures (chloroform–methanol (MeOH) and chloroform–dimethyl sulfoxide) were obtained from the corresponding solutions by mixing volumes of each solvent at room temperature in the following ratios: 1:5; 2:4; 3:3; 4:2 and 5:1. The solvents employed were all spectrophotometric grade. The multiple regression analysis of the absorption and emission maxima was carried out with the Origin Pro 7.5 software.

Results and discussion

Solvent effects on the absorption and fluorescence spectra

The solute–solvent interactions can be analyzed by examining electronic absorption and emission spectra in a variety of solvents. The absorption and fluorescence spectra of a siloxane anthraquinone derivative (PQI) were determined in non-polar and polar solvents of various polarities. The absorption and emission maxima, Stokes shifts as well as some solvent parameters (refractive index, *n*, and dielectric constant, ε, [7,18]) are listed in Table 1. The absorption spectrum of PQI shows a broad absorption band centered at about 481 nm for DMF (Fig. 2). It is observed from Table 1 that the absorption maximum exhibits a moderate shift to shorter wavelengths with increasing solvent polarity.

The effect of solvent on the fluorescence spectra of siloxane derivative has been reported in Fig. 3. In all solvents the vibrational structure is present. The first emission band was located between 537 and 543 nm. The 0–0 transition band for emission appears at 561 nm in non-polar hexane while it exhibits a bathochromic shift as the solvent dielectric constant values increase (Table 1). The position of the third emission band was in spectral range 611–617 nm. In chlorinated solvents ($CHCl_3$ and dichloroethane (DCE)) the third band become better evidenced. On increasing solvent polarity, the absorption and emission bands become broader and lost from their vibrational structure. Such behavior indicated that the stabilization of highly dipolar excited state in polar solvents. Also, the values of Stokes shift ($\Delta\tilde{\nu}$), i.e. the difference

Table 1
Some solvent parameters, spectral and photophysical characteristics of siloxane polyquinoneimine in different solvents.

No.	Solvent	n	ε	$\tilde{\nu}_{abs}$ (cm^{-1})	$\tilde{\nu}_{em}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})	Φ (%)
1	Hexane	1.3749	1.89	20.619	17.825	2794	12.85
2	Heptane	1.3878	1.92	20.619	17.794	2825	13.63
3	Dioxane	1.4224	2.22	20.833	17.452	3381	8.46
4	Toluene	1.4970	2.37	20.534	17.065	3469	4.48
5	Chloroform	1.4459	4.81	20.619	17.574	3044	12.68
6	Ethyl Acetate	1.3723	6.02	20.833	17.637	3196	10.93
7	Dichloroethane	1.4448	10.42	20.661	17.513	3148	12.67
8	Butanol	1.3993	17.51	20.704	17.668	3036	10.88
9	Acetone	1.3588	20.70	20.877	17.606	3271	10.78
10	Ethanol	1.3611	24.55	20.790	17.668	3122	9.77
11	Methanol	1.3288	33.00	20.833	17.683	3150	9.21
12	DMF	1.4305	36.71	20.790	17.422	3368	4.47
13	Acetonitrile	1.3442	37.50	20.921	17.606	3315	8.85
14	DMSO	1.4793	47.24	20.833	17.218	3336	4.91
15	Formamide	1.4470	110.00	20.747	17.391	3356	18.90

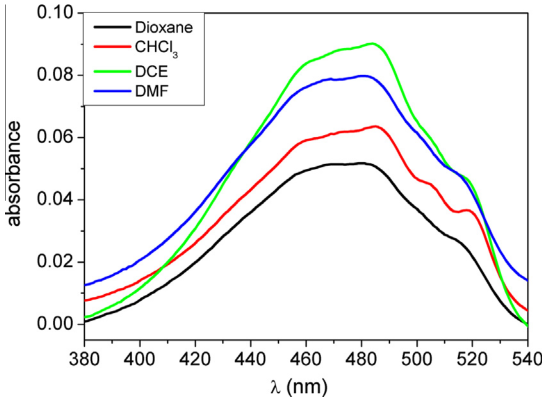

Fig. 2. UV–Vis absorption spectra of the siloxane PQI in different solvents.

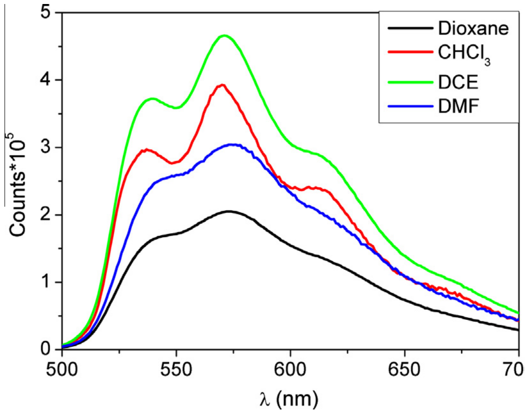

Fig. 3. Fluorescence spectra of the siloxane PQI in different solvents.

between the wavenumbers of absorption ($\tilde{\nu}_{abs}$) and fluorescence ($\tilde{\nu}_{em}$) maxima, increases on changing solvents from nonpolar to polar one (Table 1). The influence of solvent polarity on the emission maximum is more intensive than that on the electronic absorption spectrum due to the fact that the excited state is more polar than the ground state and thus higher values of the dipole moment in the excited state are expected.

The solvent dependence of the absorption and emission band maxima was investigated by using the Lippert–Mataga [19,20] and Bakhshiev [8,21] equations:

$$\Delta\tilde{\nu} = \left[\frac{2(\mu_g - \mu_e)^2}{hca_o^3}\right] F_1(\varepsilon, n) + \text{const} \tag{1}$$

$$\Delta\tilde{\nu} = \left[\frac{2(\mu_g - \mu_e)^2}{hca_o^3}\right] F_2(\varepsilon, n) + \text{const} \tag{2}$$

where μ_g and μ_e denotes the dipole moments of the molecule in ground and excited states, h is Planck constant, c is the speed of light, a_0 is the Onsager cavity radius, ε and n are the dielectric constant and refraction index of the solvents, respectively.

$F_1(\varepsilon, n)$ is the orientation polarizability function defined as:

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right] \tag{3}$$

$F_2(\varepsilon, n)$ is the solvent polarity function:

$$F_2(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \tag{4}$$

The plots of Stokes shifts ($\Delta\tilde{\nu} = \tilde{\nu}_{abs} - \tilde{\nu}_{em}$) *versus* $F_1(\varepsilon, n)$ and $F_2(\varepsilon, n)$ are given in Fig. 4. As it can be seen in Fig. 4 a linear trend for $\Delta\tilde{\nu}$ *versus* $F(\varepsilon, n)$ with a good correlation coefficient ($r > 0.91$) was obtained. However, in this correlation the following solvents were excluded: dioxane, toluene, ethanol and dimethyl sulfoxide. The deviation from linearity shows that dielectric solute–solvent interactions cannot explain the resulting solvatochromic shifts for the molecule under study, which suggests that specific solute–solvent interactions such as hydrogen bondings or dipole–dipole interactions can occur in solution.

The solvent dependence of the spectral characteristics of a molecule ($\tilde{\nu}_{abs}$, $\tilde{\nu}_{em}$, $\Delta\tilde{\nu}$) can be analyzed with the multilinear regression using the following relation:

$$y = y_o + aA + bB + cC \tag{5}$$

where y denotes the corresponding spectral property (wavenumbers in the absorption and fluorescence maxima or Stokes shift), y_o is the intrinsic spectral property in the gas phase, A, B, C are the solvent parameters and a, b, c are the coefficients of each parameter that determine the contribution of the solvent parameters to the spectral property of the molecule.

Two sets of solvent parameters were chosen to carried out the multilinear regression: Kamlet–Taft solvent parameters [22] and Catalan solvent parameters [23] and the multilinear regression can be described by the following equations:

$$Y = y_o + a\alpha + b\beta + c\pi^* \ \text{(Kamlet-Taft)} \tag{6}$$

$$y = y_o + aSA + bSB + cSP + dSdP \ \text{(Catalan)} \tag{7}$$

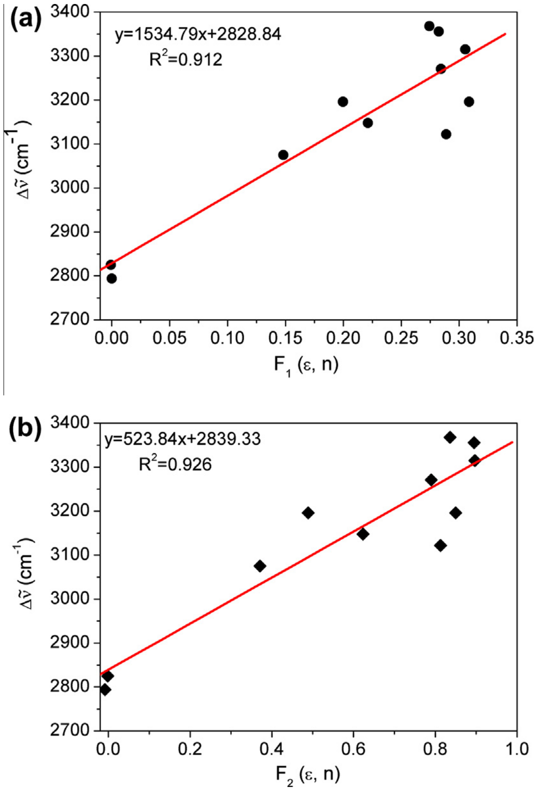

Fig. 4. Plots of $\Delta\tilde{\nu}$ *versus* $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$ for PQI in different solvents.

where α is the solvent acidity, β is the solvent basicity, π^* is an index of the solvent dipolarity/polarizability being a measure of solvent ability to stabilize a charge or a dipole by virtue of its dielectric effect, *SA* and *SB* correspond to the Kamlet–Taft parameters α and β, *SP* and *SdP* represent solvent polarizability and solvent dipolarity, respectively, *a*–*d* are the regression coefficients describing the sensitivity of the respective property to the different types of solvent–solute interactions. The Kamlet–Taft and Catalan solvent parameters are listed in Table 2.

The regression coefficients obtained by multiple linear regression analysis (MLRA) are shown in Table 3. It can be established from Kamlet–Taft Eq. (6) that the $\Delta\tilde{\nu}$ depends strongly on the coefficient representing the solvent polarizability/dipolarity parameter (Table 3). A good correlation for Kamlet–Taft relation was only obtained for $\Delta\tilde{\nu}$ with $r = 0.91$. The regression analysis gives a better correlation in the case of emission ($r = 0.81$) in comparison with absorption ($r = 0.47$). The moderate correlation in the case of absorption and emission will be improved using Catalan Eq. (7), where the polarizability (SP) and dipolarity (SdP) of the solvent are not included in only one parameter. The dominant coefficient affecting the absorption emission bands of PQI (Eq. (7)) is cSP (Table 3) which shows that the polarizability of the environment around the chromophore is the main factor determining the solvent effect on the spectral maxima. The large (negative) coefficient of SP indicates that $\tilde{\nu}_{abs}$ and $\tilde{\nu}_{em}$ are mainly controlled by solvent polarizability. The Stokes data according to Eq. (7) show that solvent dipolarity becomes the most important parameter influencing the $\Delta\tilde{\nu}$ change, followed by solvent polarizability and hydrogen bond donor ability. Otherwise, negative signs were obtained for coefficients *c* and *d* indicating a higher dipole moment in the electronically excited state.

For demonstrate a good quality of the multiple regression analysis, we ploted in Fig. 5, $\tilde{\nu}_{abs}(a)$ and $\tilde{\nu}_{em}(b)$ (experimental) *versus*

Table 2
Kamlet–Taft and Catalán parameters of employed solvents [7,22,23].

No.	Solvent	α	β	π^*	*SA*	*SB*	*SP*	*SdP*
1	Hexane	0.00	0.00	−0.08	0.000	0.056	0.616	0.000
2	Heptane	0.00	0.00	−0.08	0.000	0.083	0.635	0.000
3	Dioxane	0.00	0.37	0.55	0.000	0.444	0.737	0.312
4	Toluene	0.00	0.11	0.54	0.000	0.128	0.782	0.284
5	Chloroform	0.44	0.10	0.58	0.047	0.071	0.783	0.614
6	Ethyl acetate	0.00	0.45	0.55	0.000	0.542	0.656	0.603
7	Dichloroethane	0.00	0.10	0.81	0.030	0.126	0.771	0.742
8	*n*-Butanol	0.84	0.84	0.47	0.341	0.809	0.674	0.655
9	Acetone	0.08	0.48	0.71	0.000	0.475	0.651	0.907
10	Ethanol	0.86	0.75	0.54	0.400	0.658	0.633	0.783
11	Methanol	0.98	0.66	0.60	0.605	0.545	0.608	0.904
12	DMF	0.00	0.69	0.88	0.031	0.613	0.759	0.977
13	Acetonitrile	0.19	0.31	0.75	0.044	0.286	0.645	0.974
14	DMSO	0.00	0.76	1.00	0.072	0.647	0.830	1.000
15	Formamide	0.71	0.48	0.97	0.549	0.414	0.814	1.006

Table 3
Values of regression coefficients and correlation coefficients (*r*) obtained from MLR analysis.

	y_0 (cm⁻¹)	*a*	*b*	*s*	*d*	*r*	*n*
Kamlet–Taft							
$\tilde{\nu}_{abs}$	20.616	−54.67	234.46	76.48	–	0.467	14[a]
$\tilde{\nu}_{em}$	17.818	111.99	−57.30	−412.21	–	0.818	13[b]
$\tilde{\nu}_{\Delta v}$	2843	−76.95	117.71	473.51	–	0.914	13[b]
Catalán							
$\tilde{\nu}_{abs}$	21.131	−144.08	46.27	−860.51	323.76	0.937	14[a]
$\tilde{\nu}_{em}$	18.730	69.14	−90.43	−1421.46	−188.14	0.904	13[b]
$\tilde{\nu}_{\Delta v}$	2687	−167.87	33.50	155.29	523.29	0.924	13[b]

[a] Dioxane was excluded from correlations.
[b] Dioxane and toluene were excluded from correlations. *n* is number of solvents.

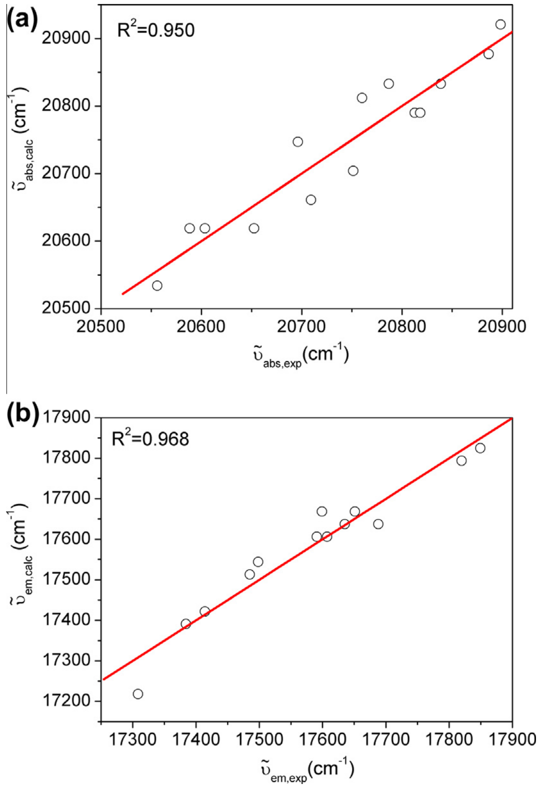

Fig. 5. Relationship between the experimental and calculated absorption (a) and emission (b) maxima, with regression coefficients obtained by multilinear regression analysis, using the Catalán equation.

$\tilde{\nu}_{abs}(a)$ and $\tilde{\nu}_{em}(b)$ (calculated). The values of correlation coefficients ($R^2 > 0.95$) confirm the good quality of the results.

Behavior of PQI in binary liquid mixtures

The behavior of a solute in a neat solvent is very different than that in mixed binary solvent mixtures, where solute may induce changes in the system composition, namely various ratios of the solvents in the solvation shell compared to that in the bulk leading to preferential solvation. If the binary mixture is considered as an ideal system (solvent–solvent interactions are negligible) then the wavenumber maximum of the solute can be expressed by the linear additive model [24–26]:

$$\tilde{\nu}_{12id} = X_1\tilde{\nu}_1 + X_2\tilde{\nu}_2 \tag{8}$$

where X_1 and X_2 are the mole fraction of solvents 1 and 2; $\tilde{\nu}_1$, $\tilde{\nu}_2$, $\tilde{\nu}_{12}$ are the PQI values of wavenumber maximum ($\tilde{\nu}_{\max}$) in the solvents 1, 2, and in the binary mixtures, respectively.Thus, in binary systems considering solvent–solvent interactions and that the solvent is different distributed in the bulk and the solvation shell of the solute [24–29], wavenumber maximum ($\tilde{\nu}_{\max}$) can be expressed by:

$$\tilde{\nu}_{12} = X_1^L\tilde{\nu}_1 + X_2^L\tilde{\nu}_2 \tag{9}$$

where X_1^L and X_2^L are the mole fraction of solvents 1 and 2 in the solvation shell of the solute, respectively. X_1^L and X_2^L can be calculated from experimental measurements by the following expressions:

$$X_2^L = \frac{\tilde{\nu}_{12} - \tilde{\nu}_1}{\tilde{\nu}_2 - \tilde{\nu}_1} = 1 - X_1^L \tag{10}$$

$$X_1^L + X_2^L = 1 \tag{11}$$

In order to quantify the extent of preferential solvation, a parameter δ_{s2} defined as Eq. (12) [24] was used:

$$\delta_{s2} = X_2^L - X_2 \tag{12}$$

A positive value of δ_{s2} indicates a preference for solvent 2 over solvent 1, while a negative value of δ_{s2} signifies the opposite [24,27].

Other criteria used to assess the type and degree of deviation from the ideality is the preferential solvation constant K_{PS}, according to model given by Frankel et al. [30]:

$$K_{PS} = \frac{X_1^L/X_2^L}{X_1/X_2} \tag{13}$$

$K_{PS} < 1$ shows a preference for solvent 1 over solvent 2 and $K_{PS} > 1$ denotes the opposite trend [30].

Absorption and emission spectra of PQI were investigated in $CHCl_3$–MeOH and $CHCl_3$–DMSO mixtures over various proportions. The absorption spectra of PQI in $CHCl_3$, MeOH and various proportions of their mixtures are depicted in Fig. 6. The absorption maximum intensity progressively decreases with increasing of content in methanol (cosolvent) of the system. A similar trend is observed in absorption spectra for $CHCl_3$–DMSO mixture (Table 4).

Fig. 7 shows the emission spectra of the PQI measured in $CHCl_3$, DMSO and their mixtures. The fluorescence intensity decreases with an increase in the concentration of the cosolvent (DMSO). A similar behavior in the emission spectra of PQI in $CHCl_3$–MeOH solvent mixtures was observed. Changes in the emission intensity with various concentrations of cosolvents indicate a modification of microenvironment of PQI in the presence of cosolvents. This behavior can be influenced by the difference in viscosity of the systems and by conformational changes. These results suggest that in studied binary liquid systems the cosolvents can determine a quenching effect on emission intensity as a function of cosolvent content.

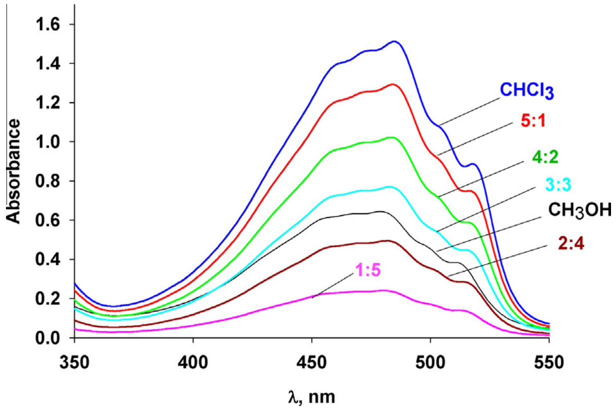

Fig. 6. Optical absorption spectra of PQI in $CHCl_3$–MeOH binary mixture.

Table 4
Absorption and emission spectral data of PQI in binary solvent mixtures.

X_2, (cosolvent)	PQI			
	Abs		Fluor	
	$\tilde{\nu}_{12}$ (cm^{-1})	$\tilde{\nu}_{12}id$ (cm^{-1})	$\tilde{\nu}_{12}$ (cm^{-1})	$\tilde{\nu}_{12}id$ (cm^{-1})
PQI in $CHCl_3$–MeOH mixture				
0	20.619	20.618	17.574	17.574
0.283	20.746	20.679	17.652	17.605
0.497	20.746	20.725	17.667	17.628
0.664	20.703	20.761	17.636	17.646
0.798	20.661	20.789	17.590	17.661
0.908	20.661	20.813	17.590	17.673
1	20.833	20.833	17.683	17.683
PQI in $CHCl_3$–DMSO mixture				
0	20.618	20.618	17.574	17.574
0.184	20.746	20.658	17.361	17.524
0.360	20.703	20.696	17.421	17.475
0.530	20.703	20.732	17.452	17.429
0.693	20.661	20.767	17.482	17.385
0.849	20.661	20.801	17.513	17.342
1	20.833	20.833	17.218	17.218

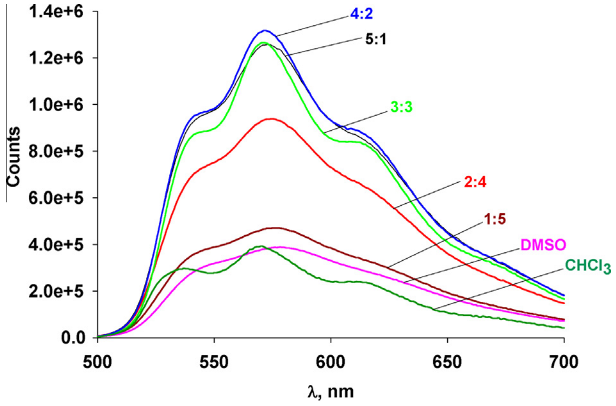

Fig. 7. Emission spectra of PQI in $CHCl_3$–DMSO binary mixture.

The binary liquid solvents exert an influence on the emission spectra, changing their shape, and spectral maxima positions. The bathochromic shifts in the emission maxima indicate no significantly structural changes of the studied samples in presence of cosolvents. The emission spectrum of the compound PQI in pure DMSO displayed only one broad band (Fig. 7). With increasing ratio of chloroform this broad band is slightly split and a new emission band (λ_{em}) appearing at 571 nm, upon excitation at 485 nm, while its fluorescence intensity increased with the increasing concentration of chloroform. Spectral data of PQI in single solvent, $CHCl_3$, MeOH, DMSO (when $X_2 = 0$ or 1) and their binary solvent mixtures at various compositions are listed in Table 4.

Fig. 8 presents the variation of $\tilde{\nu}_{12}$ with X_2 for PQI. The deviation $\tilde{\nu}_{12}$ from linearity can be interpreted as preferential solvation of PQI by one of components from the mixture and discussed in term of the effect of changing solvent proportions in binary solvent mixtures. Both positive and negative deviations from ideality have been observed for $CHCl_3$–MeOH and $CHCl_3$–DMSO binary mixed solvents and can be due to intermolecular interactions from solutions. The behavior is similar in studied binary solvent mixtures but the values of crossover point from negative to positive deviation from ideal behavior are different ($X_2 = 0.6$ for $CHCl_3$–MeOH and $X_2 = 0.4$ for $CHCl_3$–DMSO, respectively). This can be attributed to different values for solvent acidity constant of the cosolvent ($\alpha_{MeOH} = 0.93$ and $\alpha_{DMSO} = 0.0$ [7]) and their contribution to solvatochromism.

PQI is preferentially solvated by MeOH or DMSO in chloroform rich region and by chloroform at high concentration of MeOH or DMSO. Preferential solvation parameter calculated from experimental data is listed in Table 5 and also, confirms this conclusion (positive value of δ_{s2} indicate a preference for MeOH or DMSO over chloroform, for mixtures with $X_2 < 0.4$; while a negative value of δ_{s2} signifies the opposite. The values of $K_{PS} < 1$ show a preference for chloroform over solvent MeOH or DMSO and $K_{PS} > 1$ denotes the opposite trend). Similar behavior was observed for some siloxane polyazomethines previously studied [31], where the segments phenylene-ester were replaced with 1,3-bis(propylene).

Table 5
Preferential solvation parameters for PQI in binary solvent mixtures.

X_2	X_2^L		δ_{s2}		K_{PS}	
	Abs	Fluor	Abs	Fluor	Abs	Fluor
$CHCl_3$–MeOH						
0						
0.283	0.597	0.713	0.314	0.429	3.755	6.286
0.497	0.597	0.856	0.100	0.359	1.502	6.034
0.664	0.397	0.569	– 0.266	– 0.094	0.333	0.670
0.798	0.198	0.142	– 0.599	– 0.656	0.062	0.041
0.908	0.198	0.142	– 0.709	– 0.766	0.025	0.016
1						
$CHCl_3$–DMSO						
0						
0.184	0.597	0.588	0.413	0.404	6.574	6.330
0.360	0.397	0.421	0.036	0.060	1.168	1.292
0.530	0.397	0.338	– 0.132	– 0.192	0.584	0.452
0.693	0.198	0.253	– 0.494	– 0.439	0.109	0.150
0.849	0.198	0.169	– 0.651	– 0.679	0.043	0.036
1						

Solvent effects on the fluorescence quantum yield

The fluorescence quantum yield, Φ (%) is one of the important parameters to evaluate the performance of photoluminescent materials. Generally, the intensity of the emission spectra of fluorophores decreases with the polarity of solvents [32–35] and implicitly the values of quantum yields will be smaller in polar solvents. It can be observed that the fluorescence quantum yield values decrease with different extents as the solvent polarity is reduced (Table 1).

In toluene, DMF and DMSO the quantum yield have the lowest values (Table 1) due to the high viscosity of these solvents [17], which might restrict the flexibility of PQI molecules and simultaneously a quenching effect on the fluorescence intensity can occur. The lowest values in toluene and DMSO can be also attributed to the presence of solute–solvent interactions (toluene and DMSO were excluded from the correlations of Stokes shifts *versus* polarity functions (Fig. 4), which suggests an aggregation tendency, through intermolecular H-bonding with a higher non-radiative decay.

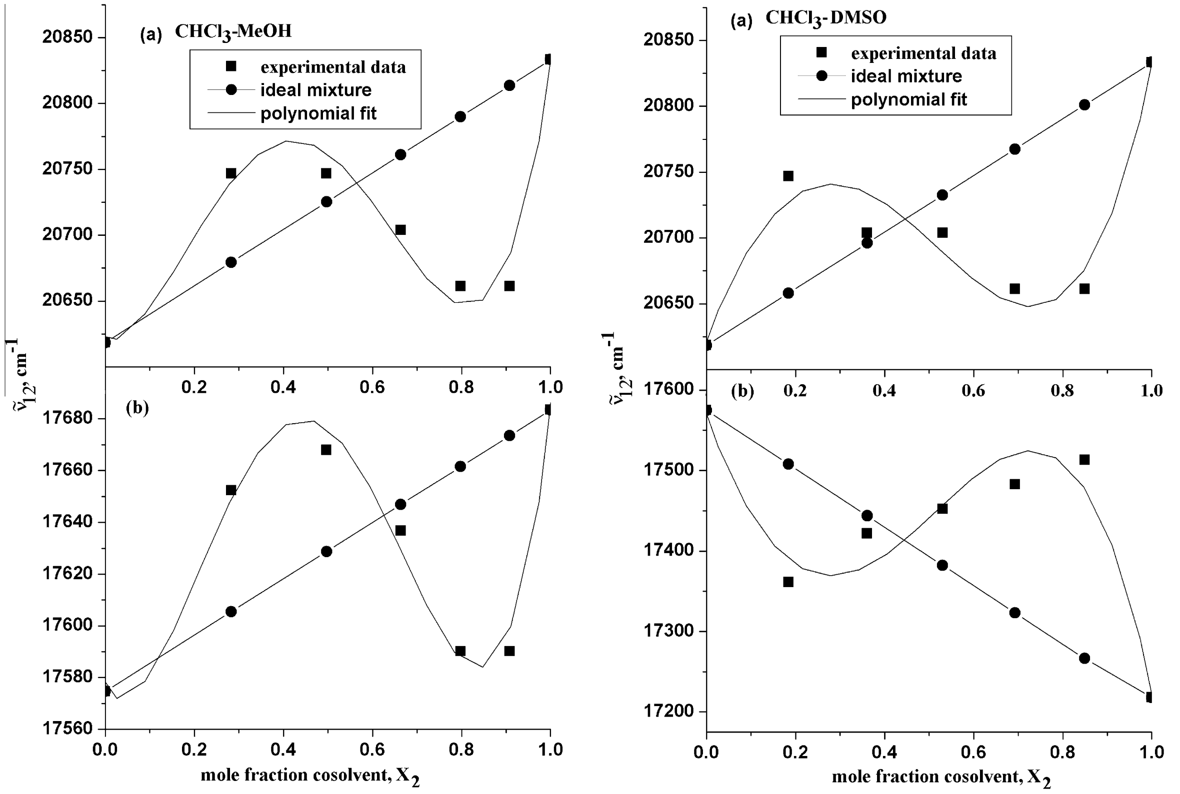

Fig. 8. Plot of $\tilde{\nu}_{12}$ as a function of the mole fraction of cosolvent for PQI in $CHCl_3$–MeOH (left) and $CHCl_3$–DMSO (right) mixed solvents (a) ground state (b) excited state. Experimental data were fitted to fourth order polynomials of the form $\tilde{\nu}_{12} = A + Bx + Cx^2 + Dx^3 + Ex^4$.

Conclusion

Solvatochromic effects, Stokes shifts, behavior in binary mixtures and the changes in quantum yield in the different solvents were analyzed for PQI. Catalan solvent scales are more appropriate than the Kamlet–Taft scales for describing the solvatochromism of siloxane derivative. Solvent polarizability is the main factor which influences the shift of absorption and fluorescence maxima, whereas the solvent dipolarity, acidity and basicity give less contributions to the spectral shifts. The emission maxima undergo a bathochromic shift with increasing solvent polarizability indicating that the excitation state is more polarizable than the ground state. The highest values of quantum yields were found in non-polar solvents (except in toluene) and in protic solvents, followed by the slightly lower values in polar solvents.

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