

Solvent effects of the electronic absorption and photophysical properties of poly(3-methoxythiophene), a conducting oligomer: evaluation of the dipole moment and specific solute–solvent interactions in the first excited singlet-state

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Received 3 August 1999; accepted 31 August 1999

Abstract

The electronic absorption and fluorescence spectra, and fluorescence quantum yields (ϕ_f) of poly(3-methoxythiophene) (PMOT) were determined at room temperature (298 K) in a variety of solvents with different polarities (hexane, cyclohexane, 2-propanol, ethyl acetate, methanol, ethanol, acetonitrile, ethylene glycol, dioxane, propylene carbonate, dimethylformamide, and dimethyl sulfoxide). The solvent effects on the PMOT spectral and photophysical characteristics (absorption and fluorescence wavenumbers) were studied quantitatively, using the Kamlet–Abboud–Taft solvation relationships. The spectral data were used, in combination with the PMOT ground-state dipole moment (μ_g), to evaluate its first excited singlet-state dipole moment (μ_e). A μ_e/μ_g ratio of 5.8 was obtained by means of the solvatochromic shift method (Bakhshiev's and Kawski–Chamma–Viallet's correlations). The Kamlet–Abboud–Taft solvatochromic parameters were applied to determine the solute–solvent interactions in the PMOT ground and excited singlet states. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(3-methoxythiophene); Excited state; Dipole moments

1. Introduction

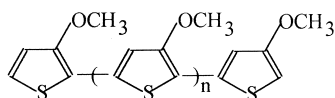
During recent years, conjugated polymers or oligomers like polythiophene and many of its derivatives have been the subject of a number of photophysical studies concerning the influence of the microstructural changes of these electro-synthesized or chemically prepared oligomer or polymer films on their luminescent spectral properties [1–5]. In contrast, little work has been devoted to the fluorescence of soluble conducting oligomers, such as substituted poly(3,4-methylenedioxybenzene) [6], poly(2-methoxy-5-alkoxy-paraphenylene) [7], poly[β -2(1-adamantyl)-2-oxo-ethoxy)naphthalene] [8] and poly[(1-methylene 2-methylnaphthalene)-*N*-pyrrole] [9], which is characterized by excimer-like emission bands in organic solutions. The possible use of conjugated polymers and oligomers in electroluminescent devices and solid-state laser materials has generated a renewed interest in the mechanistic studies

of charge injection, transport, and radiative recombination in these materials, and the evaluation of their optical and photophysical properties [10–13].

Recently, we carried out the electropolymerization of 3-methoxythiophene (MOT) in an aqueous micellar medium containing sodium dodecylsulfate (SDS) as a surfactant [14–16]. The resulting poly(3-methoxythiophene) (PMOT) film which dissolves well (mainly in its neutral form) in various organic solvents, presents electronic absorption and fluorescence spectra with remarkably distinct features as compared to the monomer. The structure of PMOT is shown in Scheme 1.

In this work, we report the influence of solvents of various polarities upon the PMOT electronic absorption and fluorescence spectra and fluorescence quantum yield, and we evaluate experimentally its dipole moment in the first excited singlet state, using Bakhshiev's and Kawski–Chamma–Viallet's solvatochromic correlations. To the best of our knowledge, this is the first time that an excited state dipole moment of a conducting oligomer has been

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$n = 3, 4$

Scheme 1.

measured. Finally, in order to determine the contribution of the different types of solute–solvent interactions in the excited state, the Kamlet–Abboud–Taft equation has been applied to our spectral data.

2. Experimental

2.1. Chemicals

Poly(3-methoxythiophene) (PMOT) films were electrosynthesized galvanostatically ($j = 1 \text{ mA cm}^{-2}$; $t = 10 \text{ min}$) in a $0.1 \text{ M MOT} + 0.1 \text{ M SDS} + 0.1 \text{ M LiClO}_4 \text{ H}_2\text{O–BuOH}$ (96/4 v/v) solution on a Pt electrode, as previously described [15]. After several treatments (see Refs. [15,16]), PMOT was recovered as a powder. MALDI-TOF mass spectrometry showed that it consisted of 73.7% hexamethoxythiophene and 26.3% pentamethoxythiophene (MW = 645 g mol^{-1}).

The solvents (hexane, cyclohexane, 2-propanol, ethyl acetate, methanol, ethanol, acetonitrile, ethylene glycol, dioxane, propylene carbonate, dimethylformamide and dimethyl sulfoxide) were spectroscopic grade (Aldrich, Acros or Sigma) and used as received.

2.2. Spectral and quantum yield measurements

The electronic absorption spectra were determined at room temperature (298 K) on a Perkin–Elmer UV–Vis spectrometer Lambda 2. The fluorescence spectra were recorded at 298 K using a Perkin–Elmer LS-50 spectrofluorometer. The excitation and emission bandwidths were 2.5 nm.

The fluorescence quantum yields were determined in the various solvents at 298 K against fluorescein as the standard ($\phi_F = 0.90$ at $25 \pm 5^\circ\text{C}$) [17]. For the ϕ_F measurements, the fluorescence spectra were recorded at 298 K on a SLM Aminco Bowman Series 2 luminescence spectrometer.

2.3. Dipole moment measurements

The ground-state dipole moment of PMOT was measured in dioxane at 293 K using a dipole meter DM-01 (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany), equipped with a DFL-2 cell as described previously [18–21]. The calibration of the instrument was carried out with six solvents of different polarities ranging from *n*-hexane to *n*-butyl ether.

Two formulae were used to determine the excited

singlet-state dipole moment of PMOT by the solvatochromic method:

Bakhshiev's formula [22]:

$$\bar{\nu}_a - \bar{\nu}_f = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} F_1 \quad (1)$$

where $\bar{\nu}_a$ and $\bar{\nu}_f$ are the wavenumbers (cm^{-1}) of electronic absorption and fluorescence emission maxima respectively, μ_g and μ_e are the permanent dipole moments in the ground and in the excited singlet state, respectively, a_0 is the Onsager cavity radius, and F_1 is defined as:

$$F_1 = \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right] \frac{2n^2+1}{n^2+2} \quad (2)$$

where D is the solvent dielectric constant and n is the solvent refractive index.

Kawski–Chamma–Viallet's formula [23,24]:

$$\frac{(\bar{\nu}_a + \bar{\nu}_f)}{2} = - \frac{2(\mu_e^2 - \mu_g^2)}{hca_0^3} F_2 \quad (3)$$

where the meaning of the symbols is the same as in Eqs. (1) and (2), except for F_2 which is defined as follows:

$$F_2 = \frac{2n^2+1}{2(n^2+2)} \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right] + \frac{3(n^4-1)}{2(n^2+2)^2} \quad (4)$$

3. Results and discussion

3.1. Solvent effects on the absorption and fluorescence spectra and quantum yields

The electronic absorption spectra, the fluorescence excitation and emission spectra, and the quantum yields of PMOT, were measured in different solvents of various polarities and hydrogen bonding abilities (Table 1). Examples of absorption and fluorescence emission spectra of $1.75 \times 10^{-5} \text{ M}$ PMOT in hexane and in DMSO are given in Figs. 1 and 2.

The electronic absorption spectra showed three or four relatively strong bands ($\epsilon \sim 5950\text{--}28850 \text{ l mol}^{-1} \text{ cm}^{-1}$), occurring at 219–221 nm (λ_1), 262–274 nm (λ_2), 333–338 nm (λ_3) and 471–487 nm (λ_4), according to the solvent used. The first two bands, which are also present in the monomer (3-methoxythiophene), have been attributed to a charge transfer transition from the methoxy group oxygen atom to the thiophene ring [25] and to the thiophene ring local $\pi \rightarrow \pi^*$ transition [26], respectively. The third band (λ_3), characterized by slightly lower molar absorption coefficients, can be ascribed to a polarized transition, parallel with the long molecular axis [11,27]. The longest wavelength peak (λ_4) is attributed to the delocalized $\pi \rightarrow \pi^*$ electronic transition, corresponding to the conjugated segments in the oligomer chain [11]. The two latter bands are markedly red-shifted relative to the corresponding bands

Table 1
Electronic absorption and fluorescence properties of PMOT in different solvents

Solvent ^{a,b}	Electronic absorption maxima					Photophysical properties			
	λ_1 , nm (ε_1) ^c	λ_2 , nm (ε_2)	λ_3 , nm (ε_3)	λ_4 , nm (ε_4)	FWHM _A ^d (cm ⁻¹)	λ_{ex} ^e (nm)	λ_{em} ^e (nm)	FWHM _F ^d (cm ⁻¹)	ϕ_F ^f
Hexane	221 (16 040)	264 (7700)	335 (5980)	471 (12250)	6666	463	545	1883	0.21
Cyclohexane	222 _s (13 920)	262 (9770)	333 (7650)	471 (15750)	6593	462	549	1921	0.20
Dioxane	–	273 (9080)	338 (10 350)	480 (12 420)	4906	464	562	1647	0.40
Chloroform	–	269 _s (12 620)	338 (10 240)	482 (17 250)	6717	461	554	1693	0.28
Ethyl acetate	–	271 (11 500)	335 (10 640)	478 (22 420)	6114	463	554	1823	0.37
2-Propanol	221 _s (22 430)	269 _s (12 530)	335 (11 210)	474 (18 980)	7728	463	559	1699	0.42
Methanol	221 (24 380)	262 (16 960)	334 (12 480)	472 (18 570)	7675	463	554	1718	0.42
Acetonitrile	219 (29 980)	265 (20 870)	334 (18 410)	476 (21 450)	8530	462	559	1633	0.45
DMF	–	274 (13 170)	337 (10 920)	484 (18 570)	8310	463	564	1592	0.43
Propylene carbonate	–	268 (13 260)	335 (12 200)	481 (19 060)	6234	NF ^g	NF ^g	NF ^g	NF ^g
Ethylene glycol	–	270 (14 840)	334 (13 450)	473 (20 300)	7693	461	562	1698	0.44
Ethanol	–	265 (14 200)	336 (12 880)	477 (19 950)	5535	461	560	1646	0.44
DMSO	–	274 (11 670)	338 (11 380)	487 (18 050)	6651	465	565	1676	0.38

^a The PMOT concentration was 1.75×10^{-5} M.

^b Solvents are listed in order of the increasing dielectric constant values.

^c ε is the molar absorption coefficient ($l \text{ mol}^{-1} \text{ cm}^{-1}$).

^d FWHM: full-width-at-half-maximum of the band.

^e λ_{ex} and λ_{em} indicate the excitation and emission wavelengths (precision: ± 1 nm).

^f ϕ_F : fluorescence quantum yield of PMOT (precision: ± 0.02).

^g NF: no fluorescence detected in this solvent; the subscripts A, F and s refer to absorption, fluorescence and shoulder, respectively.

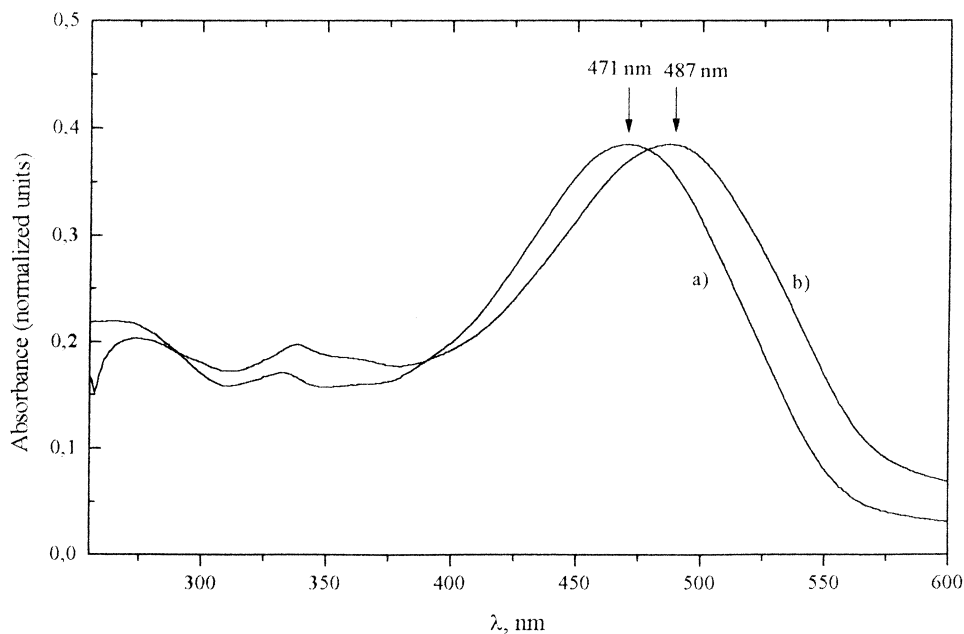


Fig. 1. Solvent effect on the absorption spectra of PMOT 1.75×10^{-5} M in (a) hexane; (b) DMSO.

in unsubstituted hexathiophene (315 and 430 nm in dioxane [11]), which indicates a more pronounced electronic delocalization in hexa(3-methoxythiophene) resulting from the electron-donating effect of the methoxy group.

Table 1 shows that λ_1 and λ_3 are not solvent sensitive. In contrast, the $\pi \rightarrow \pi^*$ electronic transitions (λ_2 and λ_4) are red-shifted with changing solvent polarity. λ_2 and λ_4 undergo a 12 and 16 nm red-shift, respectively, when going from a nonpolar solvent (cyclohexane) to a more polar one (DMSO).

The fluorescence excitation spectra exhibit a broad band

located between 461 and 465 nm, which is homothetic to the longest-wavelength absorption band. The excitation spectra exhibit a small blue-shift with respect to the absorption maxima, but no significant solvent effect is observed. In contrast, the fluorescence emission spectra are characterized by a well-defined peak which is strongly red-shifted from 545 to 565 nm on going from hexane to DMSO. This bathochromic shift reflects the occurrence of $\pi \rightarrow \pi^*$ electronic transitions in the PMOT singlet excited state.

The fullwidth-at-half-maximum (FWHM) of the bands which are comprised in a narrow range ($1750 \pm 170 \text{ cm}^{-1}$)

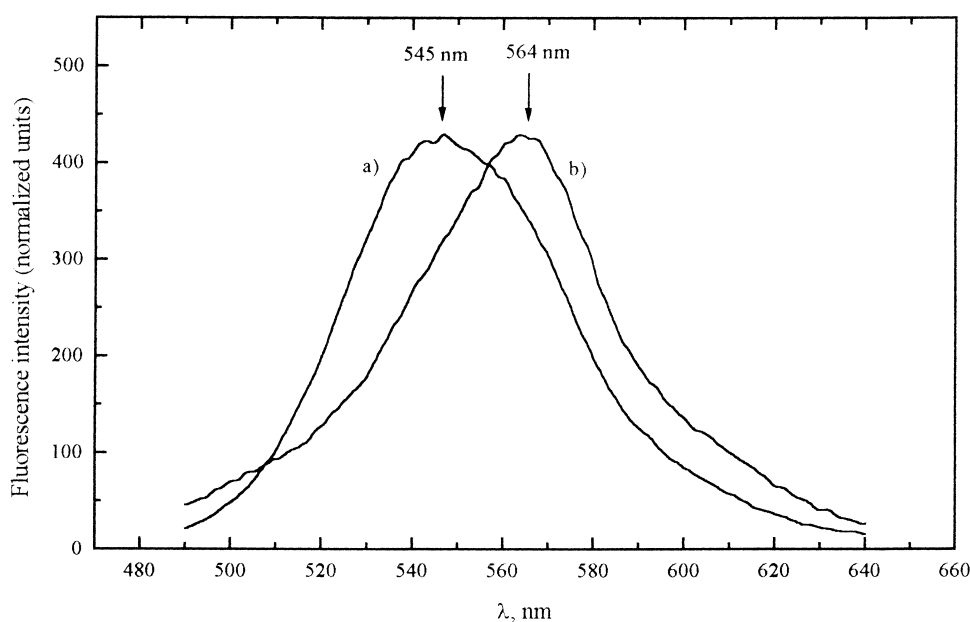
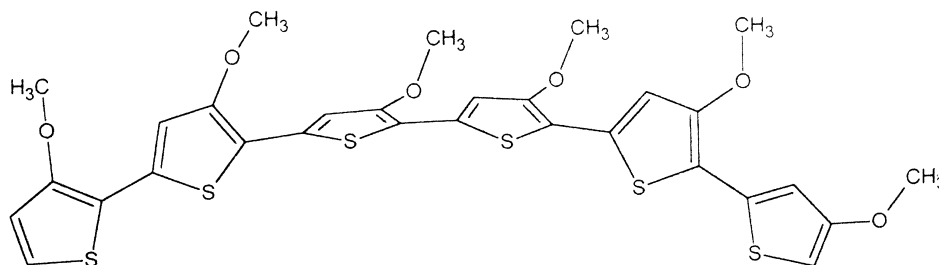


Fig. 2. Solvent effect on the fluorescence emission spectra of PMOT 1.75×10^{-5} M in (a) hexane; (b) DMSO.



Scheme 2.

for the fluorescence and a larger one ($6720 \pm 1810 \text{ cm}^{-1}$) for the absorption spectra indicate that the sharpness of the curves is also slightly solvent-dependent and that more conformers are present in the ground state than in the excited singlet state. These results also suggest that the relaxed excited singlet state produces more planar conformations than noted in the ground state, yielding a narrower distribution of conformers. Similar results have been reported in the literature for other oligothiophenes [13].

As shown in Scheme 2, the optimized geometry of PMOT conformation—calculated using Gaussian 94—seems to be nonplanar. The methoxy group was assumed to be in the same side of each thiophene ring. This is the most likely configuration, as indicated by the literature data on other 3-substituted oligothiophenes [28,29].

The PMOT fluorescence quantum yields (ϕ_F) have also been measured in the solvents under study (Table 1). The methoxy group substituent effect is not easy to discuss because the fluorescence quantum yields of oligothiophenes have been rarely investigated [11–13]. However, the ϕ_F values recently reported in the literature for hexathiophene (0.35–0.45 [11], 0.44 [12] in benzene and 0.41 [12] in dioxane) are generally greater than ours when comparing the ϕ_F data in solvents of similar polarities (for instance,

$\phi_F = 0.21$ and 0.20 for PMOT in hexane and in cyclohexane, respectively). This significant decrease of the PMOT fluorescence quantum yield may be due to the increase in the nonradiative fluorescence decay rate constant resulting from twisted conformations of this oligothiophene derivative; a similar effect has been observed in alkyl-substituted oligothiophenes [13].

Another interesting feature of the PMOT fluorescence quantum yields is that they are very sensitive to the solvent. Indeed, the ϕ_F values vary between 0.19 for hexane and 0.45 for acetonitrile. This is in contrast with the fluorescence quantum yields of unsubstituted thiophene oligomers, ranging from bithiophene to pentathiophene, which are not solvent-dependent, although their spectral wavenumbers are weakly sensitive to the solvent [12]. In the case of PMOT, the variation of the ϕ_F with the solvent may be due to specific solute–solvent interactions in the excited singlet state, related to the presence of the methoxy group.

3.2. Evaluation of the dipole moments

We used the long-wavelength absorption band (λ_4) and fluorescence emission maximum wavelengths for the quantitative studies of the solvent effects.

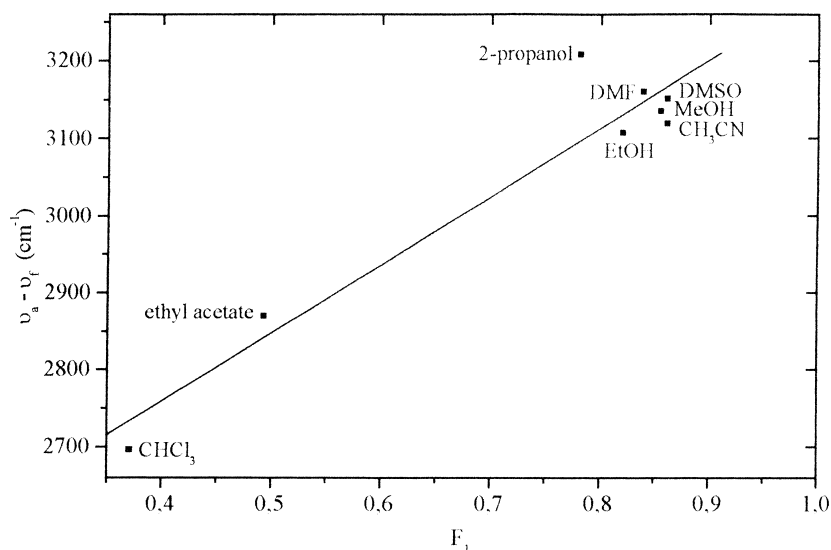


Fig. 3. Bakhshiev correlation between the solvent spectral shifts and the F_1 solvent polarity function.

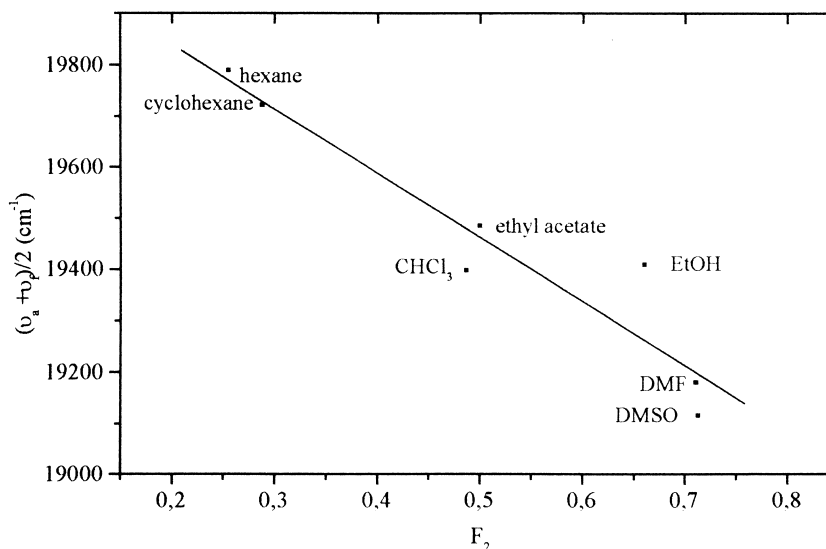


Fig. 4. Kowski–Chamma–Viallet correlation between the solvent spectral shifts and the F_2 solvent polarity function.

To determine the excited singlet state dipole moment, we plotted the Stokes shifts $(\bar{\nu}_a - \bar{\nu}_f)$ and $(\bar{\nu}_a + \bar{\nu}_f)/2$ against the solvent polarity functions F_1 and F_2 , respectively (Figs. 3 and 4). The results of the statistical treatment of Bakhshiev's and Kowski–Chamma–Viallet's correlations are satisfactory (Table 2). Indeed, a good linearity was obtained for the majority of the solvents, with correlation coefficients larger than 0.95. A positive solvatochromic behavior can be deduced from the slopes of Bakhshiev and Kowski–Chamma–Viallet linear plots.

From Eqs. (1) and (3), the slopes S_1 and S_2 of the linear graphs corresponding to Bakhshiev's and Kowski–Chamma–Viallet's correlations are, respectively:

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (5)$$

Table 2

Statistical treatment of the Bakhshiev and Kowski–Chamma–Viallet correlations of the solvent spectral shifts

Type of correlation ^a	Slope (cm ⁻¹)	Intercept (cm ⁻¹)	<i>r</i>	<i>n</i>
Bakhshiev	884	2405	0.956	8 ^b
Kowski–Chamma–Viallet	-1254	20 091	0.951	7 ^c
μ_g^d (D)	1.68			
μ_e^e (D)	9.74			

^a Solvent constant dielectric and refractive index values are taken from Ref. [30].

^b Ethylene glycol, dioxane and hexane did not obey the Bakhshiev correlation.

^c Ethylene glycol, dioxane and acetonitrile did not obey the Kowski–Chamma–Viallet's correlation.

^d Ground state dipole moment, measured with a dipole meter.

^e Excited singlet state dipole moment, obtained from a combination of the Bakhshiev's and the Kowski–Chamma–Viallet's correlations (see Eq. (7) in the text).

and

$$S_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca_0^3} \quad (6)$$

The ratio of the first excited singlet state and the ground state dipole moments can then be calculated, using the relation [31,32]:

$$\frac{\mu_e}{\mu_g} = \left| \frac{S_1 - S_2}{S_1 + S_2} \right| \quad (7)$$

We obtained a high μ_e/μ_g ratio value of 5.8, which indicates that the PMOT dipole moment is much larger in the first excited singlet state than in the ground state. This result, which is in agreement with previous work on other heterocyclic compounds such as phenothiazines [18] and coumarins [21,31,32], shows that PMOT is much more polar in the excited singlet state than in the ground state. The high value of 9.74 found for μ_e suggests the existence of important discrepancies in the electronic charge distribution in the excited singlet state relative to the ground state [31,32]. This result confirms that an extended π electronic delocalized system is present throughout the PMOT oligomer chains, with important charged resonance structures in the excited singlet state [15,16].

3.3. Correlations with π^* , α and β solvatochromic parameters

In order to evaluate the respective contributions of the solvent polarity/polarizability, hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) abilities in the PMOT ground state and excited singlet state solute–solvent interactions, we applied the Kamlet–Abboud–Taft solvation relationship [33,34] to our electronic absorption and fluorescence spectral data and to fluorescence quantum

Table 3

Statistical treatment of the Kamlet–Abboud–Taft correlations of the absorption and fluorescence emission spectral data and fluorescence quantum yields of PMOT

	S^a	a^b	b^c	Intercept	Correlation coefficient	Number of solvents
Absorption spectral data ($\bar{\nu}_a$)	-240.4	-549.6	476.6	21 228	0.976	10 ^d
Fluorescence spectral data ($\bar{\nu}_f$)	-415.7	-240.8	35.8	18 267	0.978	9 ^e
Fluorescence quantum yield ($\ln \phi_f$)	0.935	-0.205	0.421	-1.601	0.969	9 ^f

^a S is the polarity/polarizability coefficient (see Eq. (6) in the text).

^b a is the HBD ability coefficient (see Eq. (6)).

^c b is the HBA ability coefficient (see Eq. (6)).

^d Chloroform and 2-propanol did not obey the correlation.

^e Methanol and dioxane did not obey the correlation.

^f Methanol, chloroform, ethyl acetate and ethylene glycol did not obey the correlation.

yields:

$$(XYZ) = (XYZ)_0 + S\pi^* + a\alpha + b\beta. \quad (8)$$

where (XYZ) is a solvatochromic property, π^* is the solvent polarity/polarizability, α and β are the solvent HBD and HBA abilities, and a and b are the corresponding regression coefficients.

We applied the method of multiple linear regression analysis, which is known to give results comparable with the stepwise method [33]. The π^* , α and β parameters were obtained from Ref. [33]. We used the wavenumbers of the $\pi \rightarrow \pi^*$ transition absorption maxima ($\bar{\nu}_a$) and of the fluorescence emission maxima ($\bar{\nu}_f$) of PMOT in various solvents.

3.4. Correlation of the absorption and fluorescence wavenumbers

The results of the Kamlet–Abboud–Taft correlations are

summarized in Table 3. The plots present a good linearity, as shown by the correlation coefficients larger than 0.97. The majority of the solvents obeyed the correlations (Figs. 5 and 6). The negative signs of S coefficients confirm that increasing the solvent polarity/polarizability (π^*) leads to a bathochromic shift of the absorption and fluorescence bands.

This demonstrates that the ground and excited singlet states of PMOT are more stabilized in polar solvents. Moreover, the S negative value, found to be larger for fluorescence than absorption data, is in agreement with the increase of PMOT dipole moment obtained in the excited singlet state. The a coefficient negative signs (and, logically, b coefficient positive signs) show that increasing the solvent HBD ability (or decreasing the solvent HBA ability) leads to a red shift in $\bar{\nu}_a$ and $\bar{\nu}_f$. This indicates that the solute–solvent hydrogen bonding formation increases for both electronic states, which stabilizes them in solvents with high HBD or low HBA abilities. Also, a and b present higher

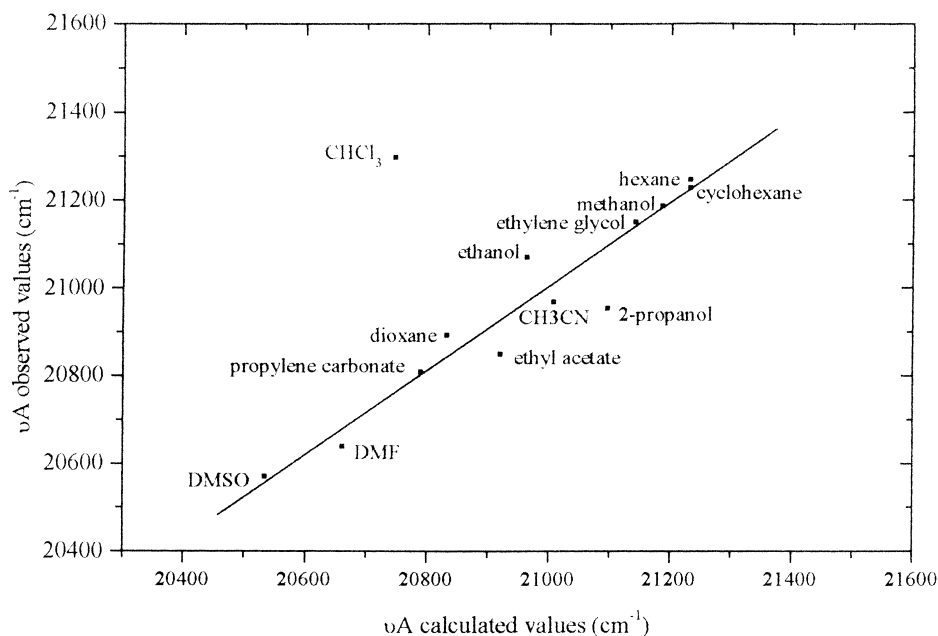


Fig. 5. Kamlet–Abboud–Taft's multiparameter solvation energy relationship for the absorption spectral data of PMOT.

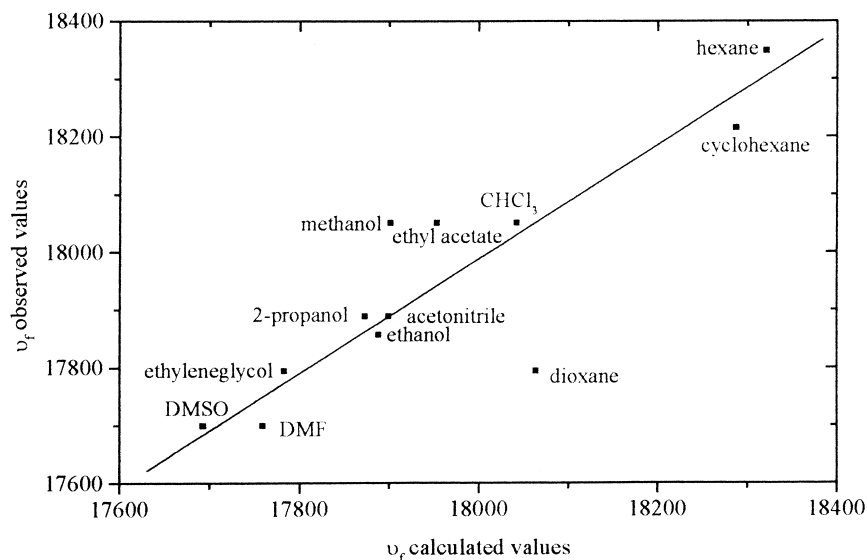


Fig. 6. Kamlet–Abboud–Taft's multiparameter solvation energy relationship for the fluorescence spectral data of PMOT.

values in the ground state than in the excited singlet state, which demonstrates that the PMOT ground state is more sensitive than the excited state to these types of interactions.

3.5. Correlation of the fluorescence quantum yields

In the course of a study of the solvent effects on the fluorescence of thioxanthone, Burget and Jacques [35] established a good correlation between $\ln(1/\phi_F - 1)$ and the Kamlet–Abboud–Taft solvatochromic parameters. $1/\phi_F - 1$ represents the ratio of the nonradiative (k_{NR}) and radiative (k_F) fluorescence decay rate constants. In this case, the variation of the fluorescence quantum yields has been

ascribed to the changes in the nonradiative processes [35,36]. We attempted to use the same type of correlation for PMOT, but the correlation coefficient was poor (0.69). In contrast, we obtained a good correlation when employing $\ln \phi_F$ (which is equal to $k_F \tau_F$, τ_F being the fluorescence lifetime of PMOT). The statistical treatment is satisfactory (Table 3). When we compute ϕ_F using this correlation, the resulting values are close to the measured ones (Fig. 7). The signs of S , a and b show that the fluorescence quantum yield is higher in the more polar and hydrogen bond acceptor solvents. For unsubstituted thiophene oligomers, it is well established that the deactivation process of S_1 state involves an intersystem crossing process and that its efficiency

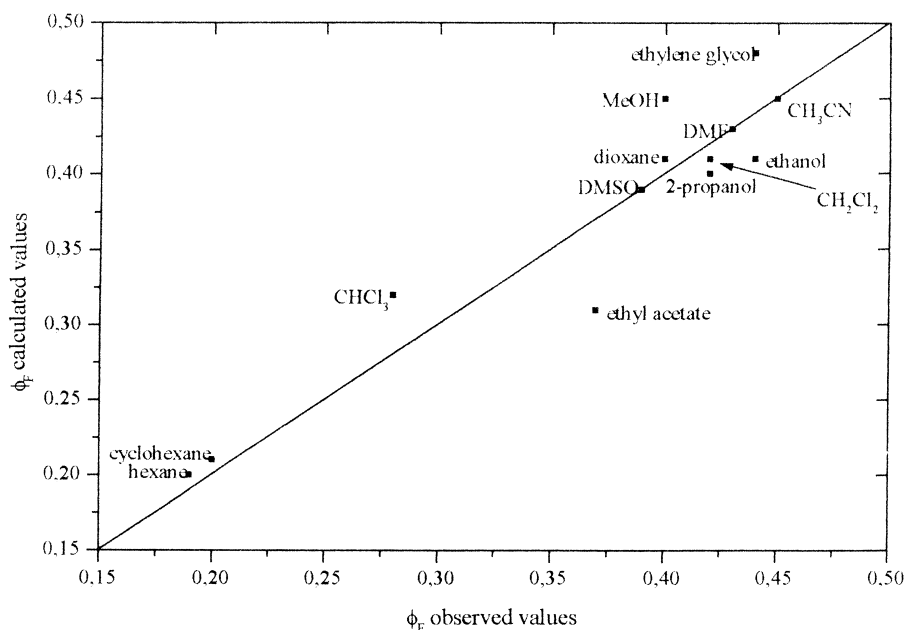


Fig. 7. Kamlet–Abboud–Taft's multiparameter solvation energy relationship for the PMOT fluorescence quantum yields.

depends on the singlet–triplet energy gap [12,13,37], which is strongly affected by the solvent characteristics [38,39]. Therefore, in the case of PMOT, the ϕ_F solvent-dependence can be attributed mainly to modifications of the lowest unoccupied molecular orbital (LUMO) energy upon changing the solvent.

4. Conclusions

We have demonstrated in this work that Bakhshiev's and Kawski–Chamma–Viallet's correlations can be used to evaluate the dipole–dipole interactions in the ground and excited singlet states of a conducting thiophene oligomer (PMOT). It was shown that the dipole moment was significantly higher in the excited singlet state than in the ground state.

The role of specific solute–solvent interactions in the solvatochromic shifts of PMOT has also been investigated, using the Kamlet–Abboud–Taft equation. This approach has shown that hydrogen-bonding abilities must be taken into account to appreciate the overall solute–solvent interactions effects on the photophysical properties of oligothiophene derivatives such as PMOT.

Acknowledgements

Modou Fall is grateful to the Third World Academy of Science (TWAS) for a grant during this work (RGA 96-265 RG/CHE/AF/AC). The authors wish to thank Omar R. Martinez (FAU) for his help with the experimental determination of the dipole moments.

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