

# Luminescence Properties of New Fused Benzothiophene Derivatives and Their Conductive Oligomers Structural and Solvent Effects\*

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The structural and solvent effects on the electronic absorption and fluorescence spectra, and fluorescence quantum yields, of four new fused benzothiophene derivatives, including benzothieno[3,2b]-thiophene (BTT), benzothieno[3,2-b]benzothiophene (BTBT), 6-methoxy[1]benzothieno[3,2b]-thiophene (MeOBTT), and benzothieno[3,2-b]indole (BTI) were investigated at 295 K. The luminescence properties of the corresponding conductive oligomers, poly(BTT) and poly (MeOBTT), electrosynthesized in acetonitrile, were also studied. Satisfactory McRae, Suppan, and Kawski-Chamma-Viallet solvatochromic correlations were established for the four monomers in most solvents. A weak negative solvatochromic behavior was found for these compounds, indicating that their dipole moments are slightly lower in the excited singlet state than in the ground state. Kamlet-Abboud-Taft multiparametric correlations were also obtained for absorption and fluorescence wave numbers and quantum yields, demonstrating the existence of specific solute-solvent interactions. In the case of the oligomers, important red-shifts of the fluorescence emission maxima ( $\Delta\lambda \approx 90\text{--}110\text{ nm}$ ) relative to the corresponding monomers were observed, which shows the extent of conjugated segments in the oligomer chains.

**KEY WORDS:** Fused benzothiophenes; conductive oligomers; luminescence; solvent effects.

## INTRODUCTION

Fused benzothiophene derivatives constitute a group of heterocyclic compounds of great potential interest

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because they possess ferroelectric liquid crystal properties [1] and they can be used to perform electrosynthesis, leading to a novel class of conducting polymers that could display important optical, electrochemical, and anticorrosive properties. As previously reported, luminescence spectroscopy is widely applied to study the microstructure, electronic delocalization, exciton formation, redox processes and solute-solvent interactions in various electroactive oligomers and polymers [2–11].

Recently, some luminescence properties of substituted oligothiophene derivatives have been investigated [6–11]. Ng *et al.* [6] have found that conducting regioregular poly[1,4-bis(3-alkyl-2-thienyl) phenylenes] were strongly fluorescent with a maximum fluorescence yield of 26% and presented a bandgap energy of 2.5 eV. The

same authors have shown that the fluorescence quantum efficiency of alternating block copolymers, incorporating 3-alkyl substituted thiophene and aniline repeat units, decreased from about 16 to 5% upon increasing pendant alkyl chain length from methyl to dodecyl, which may be explained by the concomitant decrease of the number of monomeric repeating units [7]. Sato *et al.* [8] have observed the dual photoluminescence of electro-synthesized polybithiophene and polyterthiophene thin films, with emission lifetimes in the few tens and few hundreds of picosecond suggesting the existence of at least two distinct excitons in the films, in agreement with the observation of both amorphous and microcrystalline regions.

Also, we have investigated the optical and photo-physical characteristics of poly(3-methoxy thiophene) (PMOT) films, electrochemically prepared in an aqueous anionic micellar medium and mainly constituted of hexamers [9,10]. Important solvent effects on the absorption and fluorescence spectra, and fluorescence quantum yields of PMOT, were determined, leading to quantitative solvatochromic correlations. As a result, the PMOT dipole moment was found to be significantly higher in the first excited singlet state than in the ground state, while the specific solute-solvent interactions included the contribution of notable solvent hydrogen-bond abilities [9]. Strong red-shifts of the PMOT absorption and fluorescence emission bands relative to unsubstituted sexithiophene and 3-methoxythiophene suggested a marked electronic delocalization resulting from the methoxy group electrodonating mesomer effect and an extended conjugation in the hexamer singlet excited state [10]. In addition, we have demonstrated that a significant fluorescence quenching of PMOT takes place in the presence of various quenchers; modified Stern-Volmer relationships were obtained with large bimolecular rate constants ( $2.7 \times 10^9 - 6.1 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ ), which indicates electronic energy migration throughout the PMOT hexamer repeat units [10]. In the case of electro-synthesized composite PMOT-bithiophene (BT) oligomers, electronic absorption and fluorescence spectra properties were found to depend on the bithiophene initial concentration used during electro-synthesis and on the film composition and oligomer chain length; biexponential fluorescence decays were observed [11].

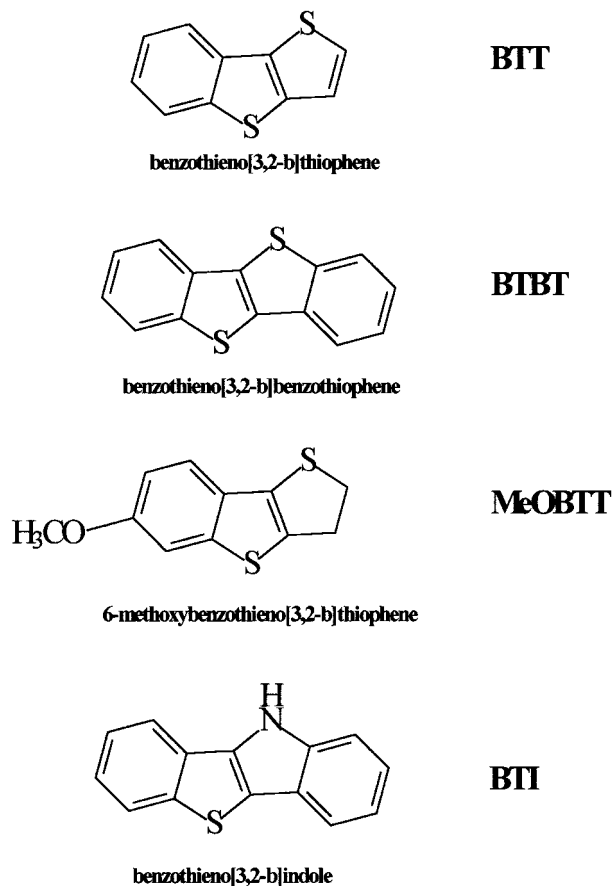
In this work we study the structural and solvent effects on the electronic absorption and fluorescence spectra, and fluorescence quantum yields of four new fused benzothiophene derivatives, including benzothieno[3,2-b]thiophene (BTT), benzothieno[3,2-b]benzothiophene (BTBT), 6-methoxy[1]benzothieno[3,2-b]thiophene (MeOBTT), and benzothieno[3,2-b]indole (BTI) at 295 K and the luminescence properties of the

corresponding electro-synthesized, conductive oligomers poly(BTT), and poly(MeOBTT) (Scheme 1). To evaluate the change of dipole moment upon electronic excitation, McRae, Suppan, and Kawski-Chamma-Viallet solvatochromic correlations are established for the four monomers in 10 solvents. Also, to determine the contribution of the different types of specific solute-solvent interactions in the excited singlet state, the Kamlet-Abboud-Taft multi-parameter relationships are applied to absorption and fluorescence spectral data. Finally, in the case of the fused benzothiophene oligomers, the fluorescence excitation and emission maxima shifts relative to the corresponding monomers are evaluated to estimate the extent of conjugated segments in the oligomer chains.

## EXPERIMENTAL

### Chemicals

Benzothieno[3,2-b] benzothiophene (BTBT) and benzothieno [3,2-b] indole (BTI) were synthesized



**Scheme 1.** Structure of the fused benzothiophene derivatives under study.

according to modified literature procedures [12]. The synthesis of benzothieno[3,2-b] thiophene (BTT) and 6-methoxy [1] benzothieno [3,2-b] thiophene (MeOBTT) is described in detail elsewhere [13]. The structure and purity of all fused benzothiophene derivatives were verified by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR, and elemental analyses. Lithium perchlorate (Acros) was used as received. Aldrich and Merck analytical or spectroscopic grade solvents (dioxane, carbon tetrachloride, toluene, chloroform, ethylacetate, dichloroethane, ethanol, acetonitrile, dimethyl sulfoxide, and dimethyl formamide) were used to prepare the solutions.

### Electrosynthesis of Oligomers

Poly (PTT) films were electrosynthesized galvanostatically ( $j = 0,5 \text{ mA/cm}^2$  during 10 min) on a Pt electrode, while poly(MeOBTT) films were electro-synthesized potentiostatically ( $E = 1.05 \text{ V/SCE}$  during 3 min, followed by successive potential scans during 30 min), as described elsewhere [13]. Poly(BTT) and poly(MeOBTT) were obtained from a 0.1 M  $\text{LiClO}_4$  acetonitrile solution containing, respectively,  $5 \times 10^{-2} \text{ M}$  of BTT and  $1 \times 10^{-2} \text{ M}$  of MeOBTT.

### Instrumentation

Electronic absorption spectra of the fused benzothiophene derivatives and their oligomers were measured on a Perkin-Elmer UV-Vis Lambda 2 spectrometer. Fluorescence excitation and emission spectra were recorded using a Perkin-Elmer LS 50 spectrofluorometer. Fluorescence quantum yields were determined on a SLM Aminco-Bowman Series 2 spectrofluorometer. All spectral measurements were performed at 295 K.

### Procedure

Electronic absorption, excitation, and emission fluorescence spectra and fluorescence quantum yields of  $2 \times 10^{-6} \text{ M}$  BTT, MeOBTT, BTBT, and BTI were carried out in 10 solvents, including carbon tetrachloride, toluene, dioxane, chloroform, ethylacetate, dichloromethane, ethanol, acetonitrile, dimethyl sulfoxide, and water. Fluorescence quantum yields were measured using quinine sulfate as a reference ( $\phi_F = 0.58$ ) [14] in a 0.05-M  $\text{H}_2\text{SO}_4$  aqueous solution. Electronic absorption and excitation and emission fluorescence spectra of poly(BTT) and poly(MeOBTT) were recorded in dimethyl formamide.

## RESULTS AND DISCUSSION

### Structural and Solvent Effects on the Absorption and Fluorescence Spectral Properties of Fused Benzothiophenes

The spectral absorption and fluorescence properties of the fused benzothiophene derivatives under study in several solvents of different polarities are given in Table I.

As can be seen, the four monomers are characterized by the presence of two well-resolved main absorption bands in the regions of 240–270 and 290–330 nm for BTBT, 245–275 and 290–315 nm for BTT, 230–270 and 310–355 nm for BTI, and 250–280 and 290–320 nm for MeOBTT. The shortest-wavelength bands, which generally have the highest molar absorption coefficients ( $\log \epsilon = 3.7\text{--}4.8$ ), can be attributed to the  $\pi \rightarrow \pi^*$   $^1\text{B}$  transitions, whereas the long-wavelength bands, with weaker, but still quite high, molar absorption coefficients ( $\log \epsilon = 3.1\text{--}4.5$ ) belong to the  $\pi \rightarrow \pi^*$   $^1\text{La}$  and  $^1\text{Lb}$  transitions. The presence of weaker shoulders at long wavelength can be ascribed to the overlapping of  $n, \pi^*$  bands due to the thiophene ring, by  $\pi, \pi^*$  bands.

Figure 1 shows that important changes of absorption spectra take place when modifying the structure of fused benzothiophenes. The fine vibrational structure of BTT, BTBT, and MeOBTT spectra is better resolved than that of BTI spectra. Moreover, significant red-shifts of the absorption band maxima occurred upon going from BTT (or MeOBTT) to BTBT and BTI, which may be related to the increase of  $\pi$  electronic conjugation throughout the series of fused benzothiophenes. Relatively weak blue-shifts of the absorption bands in the 290–355 nm region ( $\Delta\lambda_A = 3\text{--}10 \text{ nm}$ , according to the compound) were observed upon increasing the solvent polarity, which indicates a slight negative solvatochromism (Fig. 2).

The fluorescence excitation and emissions spectral characteristics of the fused benzothiophene derivatives are reported in Table I. The excitation spectra contain bands generally located at wavelength values close to those of the absorption spectra. As can be seen, BTBT and BTT exhibited two emission bands situated in the 320–360 nm region for most solvents, whereas BTI and MeOBTT presented generally only one wide emission band in the 340–375 nm region. Important red-shifts of the emission bands ( $\Delta\lambda_{em} = 34\text{--}43 \text{ nm}$ , according to the solvent) were observed when changing from BTT to BTI (Fig. 3), in the same structural order as in the case of the absorption spectra. Except for water, weak blue-shifts of the emission bands ( $\Delta\lambda_{em} = 3\text{--}9 \text{ nm}$ ,

**Table I.** Electronic Absorption and Fluorescence Excitation and Emission Spectral Properties of Fused Benzothiophene Derivatives in Various Solvents<sup>a</sup>

Compound	Solvent <sup>b</sup>	$\lambda_A$ , nm, (log $\epsilon$ ) <sup>c</sup>	$\lambda_{ex}$ , nm <sup>d</sup>	$\lambda_{em}$ , nm <sup>d</sup>	$\phi_f$ <sup>e</sup>
BTBT	Dioxane	<u>238</u> (4.33), <b>258</b> (4.45), <u>306</u> (4.57), 319 (4.37), 331 (3.95).	305	339, <u>355</u>	0.009
	Carbon tetrachloride	<b>267</b> (4.09), <u>309</u> (4.34), 334 (4.03).	306	344, <u>358</u>	0.001
	Toluene	<b>294</b> (4.64), 308 (4.52), 332 (3.92).	NF <sup>f</sup>	NF	NF
	Chloroform	<b>258</b> (4.35), 266 (4.41), <u>308</u> (4.41), 332 (4.06).	307	341, <u>357</u>	0.03
	Ethyl acetate	<b>263</b> (4.4), 293 (4.29), <u>306</u> (4.41), 330 (4.04).	301	337, <u>353</u>	0.028
	Dichloroethane	<b>265</b> (4.36), 295 (4.28), 307 (4.39), 332 (4.04).	302	341, <u>356</u>	0.031
	Ethanol	<u>237</u> (4.21), <u>254</u> (4.18), <b>263</b> , (4.31), 293 (4.27), <u>306</u> (4.35), 330 (3.98).	300	336, <u>352</u>	0.52
	Acetonitrile	255 (4.28), <b>262</b> (4.33), 273 (4.29), 293 (4.27), <u>305</u> (4.35), 329 (3.99).	303	339, <u>353</u>	0.041
	Dimethyl sulfoxide	<b>296</b> (4.28), <u>308</u> (4.39), 332 (4.06)	303	342, <u>357</u>	0.025
	Water	<u>222.5</u> (3.94), <b>262</b> (3.86), 334 (3.63), 352 (3.87).	300	358, <u>370</u>	0.013
BTT	Dioxane	<u>246</u> (4.13), 258 (4.08), <b>267</b> (4.18), 290 (4.07), 303 (3.89), 314 (3.71).	298	<u>331</u>	0.022
	Carbon tetrachloride	<b>295</b> (4.15), 305 (4.05), 316 (3.89).	294	323, <u>339</u>	0.0002
	Toluene	<b>264</b> (4.69), 279 (4.17), 295 (3.87), 315 (3.69).	NF <sup>f</sup>	NF	NF
	Chloroform	<b>268</b> (4.35), 292 (4.13), 303 (3.97), 315 (3.78).	290	321, <u>334</u>	0.025
	Ethyl acetate	<b>268</b> (4.2), 279 (4.21), 314 (4.01)	299	<u>324</u>	0.026
	Dichloroethane	<b>268</b> (4.24), 278 (4.17), 313 (4.05).	291	<u>322</u>	0.028
	Ethanol	<u>246</u> (4.22), <b>266</b> (4.22), 291 (4.11), 312 (3.94), 314 (3.77).	287	318, <u>330</u>	0.041
	Acetonitrile	<u>244</u> (3.72), <b>266</b> (4.22), 289 (4.09), 303 (3.88), 312 (3.68).	286	319, <u>331</u>	0.038
	Dimethyl sulfoxide	291 (3.5), <b>304</b> (3.34), 314 (3.15).	298	323, <u>333</u>	0.15
	Water	<u>245</u> (4.27), <b>265</b> (4.25), 289 (4.13), 313 (3.7).	286	318, <u>334</u>	0.002
BTI	Dioxane	<u>254</u> (4.48), 304 (4.25), <b>318</b> (4.22), 340 (3.86).	317	<u>368</u>	0.008
	Carbon tetrachloride	310 (4.01), <b>312</b> (4.02), 339 (3.57).	NF <sup>f</sup>	NF	NF
	Toluene	264 (4.61), <u>278</u> (4.68), 289 (4.59), <b>318</b> (4.2).	NF <sup>f</sup>	NF	NF
	Chloroform	310 (3.89), <b>318</b> (3.9), 339 (3.58).	316	<u>372</u>	0.01
	Ethyl acetate	<u>254</u> (4.09), 264 (4.07), <b>337</b> (3.87).	314	<u>364</u>	0.012
	Dichloroethane	<u>264</u> (3.95), 273 (2.89), <b>318</b> (3.36), 341 (3.3).	315	<u>365</u>	0.014
	Ethanol	<u>254</u> (4.19), 310 (4.07), <b>318</b> (4.07), 339 (3.66).	314	351, <u>367</u>	0.018
	Acetonitrile	232 (4.24), <u>252</u> (4.22), 308 (4.1), <b>316</b> (4.1), 336 (3.71).	315	<u>369</u>	0.02
	Dimethyl sulfoxide	<u>264</u> (3.68), <b>312</b> (3.64), 340 (3.48).	315	<u>371</u>	0.2
	Water	<u>250</u> (3.82), <b>339</b> (3.73), 356 (3.76).	315	<u>374</u>	0.0002
MeOBTT	Dioxane	254 (4.55), <b>266</b> (4.29), 299 (3.99), 320 (3.49).	270	<u>340</u>	0.016
	Carbon tetrachloride	<b>265</b> (3.96), <b>276</b> (4.19), 300 (4.15).	NF <sup>f</sup>	NF	NF
	Toluene	<u>279</u> (4.14), <b>297</b> (4.05).	NF <sup>f</sup>	NF	NF
	Chloroform	<b>263</b> (4.56), <u>274.5</u> (4.65), 296 (4.52), 320 (3.49).	274	<u>340</u>	0.035
	Ethyl acetate	<b>262</b> (4.89), 296 (4.8), 293 (4.2), 318 (3.77).	262	<u>341</u>	0.03
	Dichloroethane	<b>274</b> (4.16), 303 (3.63).	274	<u>339</u>	0.45
	Ethanol	<b>262</b> (4.38), <u>271.5</u> (4.5), 291 (4.25), 318 (3.84).	272	<u>338</u>	0.12
	Acetonitrile	<b>263</b> (4.69), <u>272</u> (4.78), 294 (4.57), 320 (3.96).	272	<u>341</u>	0.1
	Dimethyl sulfoxide	252 (4.57), <u>274</u> (4.72), 298 (4.46), 319 (4.12).	273	<u>341</u>	0.56
	Water	<b>262</b> (3.39), <u>271</u> (4.43), 292 (4.23), 317 (3.8).	271	<u>340</u>	0.095

<sup>a</sup> The concentrations of fused benzothiophene derivatives were  $2.10^{-6}$  M for electronic absorption and fluorescence spectra.

<sup>b</sup> Solvents are listed in the order of increasing dielectric constant.

<sup>c</sup> Absorption band wavelengths. The underlined wavelengths correspond to the maxima of the spectra. The logarithms of the molar absorption coefficients ( $M^{-1} \text{ cm}^{-1}$ ) are given in parentheses. Wavelength precision:  $\pm 1$  nm. The bold  $\lambda_A$  values were used for the solvatochromic correlations.

<sup>d</sup> Fluorescence excitation ( $\lambda_{ex}$ ) and emission ( $\lambda_{em}$ ) maxima. Wavelength precision:  $\pm 1$  nm. The underlined emission intensity maximum values were used for the solvatochromic correlations.

<sup>e</sup> Fluorescence quantum yield ( $\phi_f$ ) values measured relative to quinine sulfate.

<sup>f</sup> NF: Compound not fluorescent in this solvent.

according to the compound) were noted upon increasing the solvent polarity, which confirms the existence of a small negative solvatochromism (Fig. 4).

In contrast, the fluorescence quantum yields ( $\phi_f$ )

varied strongly from 0.0002–0.56, according to the compound and the nature of the solvent (Table I). With the exception of water, an important increase of  $\phi_f$  occurred upon increasing the solvent polarity.

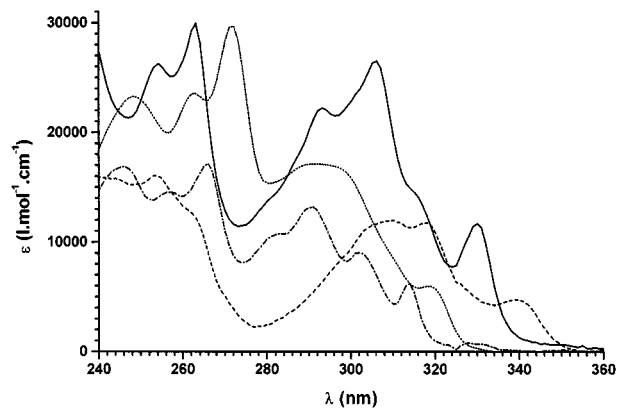


Fig. 1. Electronic absorption spectra of  $2 \times 10^{-6}$  M BTBT (solid curve), MeOBTT (·····), BTT (— · — ·), and BTI (— — —) in ethanol at 295 K.

### Solvatochromic Correlations

To determine the relative changes of the dipole moment upon going from the ground state to the singlet excited of the fused benzothiophene derivatives, we applied the solvatochromic method, using three distinct formulae.

McRae formula [16]:

$$\bar{\nu}_A = \frac{-\mu_g(\mu_e - \mu_g)}{hca_o^3} F_3 \quad (1)$$

Suppan formula [16]:

$$\bar{\nu}_A = \frac{-\mu_g(\mu_e - \mu_g)}{hca_o^3} F_4 \quad (2)$$

where  $\bar{\nu}_A$  is the wave number ( $\text{cm}^{-1}$ ) of the electronic

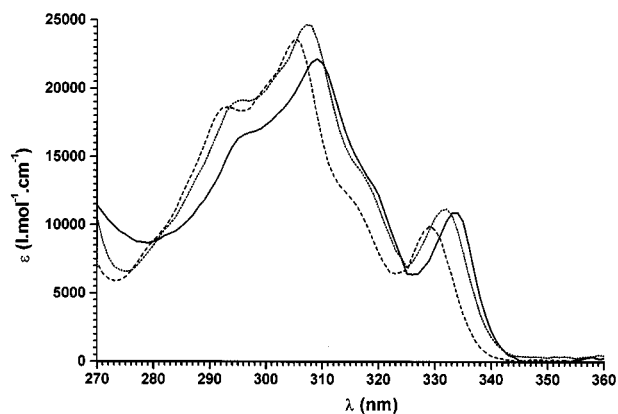


Fig. 2. Solvent effect on the electronic absorption spectra of  $2 \times 10^{-6}$  M BTBT at 295 K. Solvents: carbon tetrachloride (solid curve), dichloroethane (·····), and acetonitrile (— · — ·).

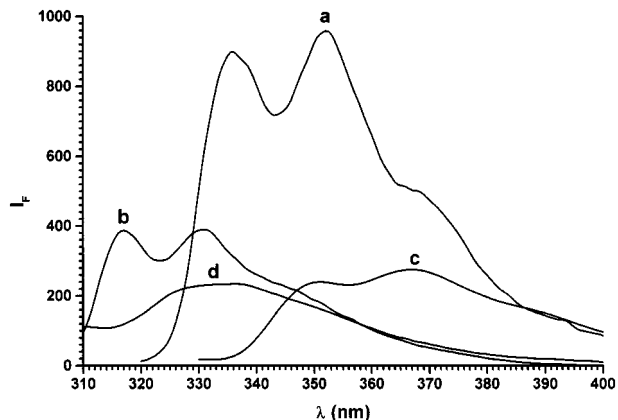


Fig. 3. Fluorescence emission spectra of  $2 \times 10^{-6}$  M BTBT (a), BTT (b), BTI (c), and MeOBTT (d) in ethanol at 295 K. Excitation wavelengths were respectively, 272 nm (MeOBTT), 300 nm (BTBT), 287 nm (BTT), and 314 nm (BTI).

absorption maxima;  $\mu_g$  and  $\mu_e$  are the permanent dipole moments in the ground and in the singlet excited state, respectively;  $h$  is the Planck constant;  $c$  is the light speed, and  $a_o$  is the Onsager cavity radius. The solvent function

$F_3$  and  $F_4$  are defined as:  $F_3 = \frac{2(D-1)}{D+2}$  and  $F_4 =$

$\frac{2(2D-1)}{2D+1}$  (with  $D$ : solvent dielectric constant).

Kawski-Chamma-Viallet formula [17]:

$$\frac{\bar{\nu}_A + \bar{\nu}_F}{2} = \frac{2(\mu_e^2 - \mu_g^2)}{hca_o^3} [F_2] \quad (3)$$

where  $\bar{\nu}_F$  is the wave number ( $\text{cm}^{-1}$ ) of fluorescence maxima and  $F_2$ , a solvent function, is defined as:

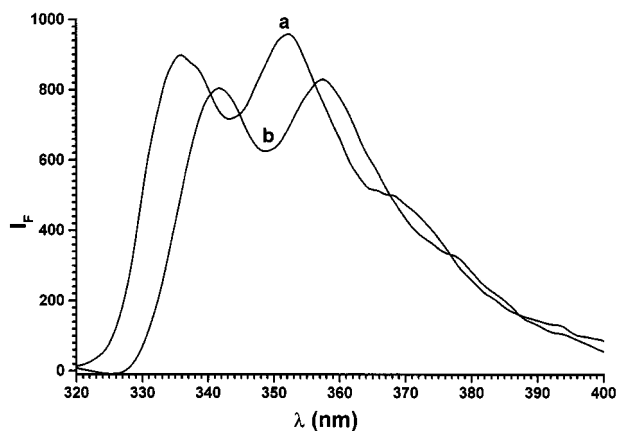


Fig. 4. Solvent effect on the fluorescence emission spectra of  $2 \times 10^{-6}$  M BTBT at 295K. Solvents: ethanol (a) and carbon tetrachloride (b).  $\lambda_{\text{exc}} = 300$  nm (a),  $\lambda_{\text{exc}} = 306$  nm (b).

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

and the meaning of the remaining symbols in Eq. (3) is the same as in Eqs. (1) and (2).

In the case of McRae and Suppan formulas, we plotted  $\bar{\nu}_A$  against the solvent functions  $F_3$  and  $F_4$ , respectively, while for Kowski-Chamma-Viallet formula, we plotted  $\frac{\bar{\nu}_A + \bar{\nu}_F}{2}$  against  $F_2$ . The  $F_2$ ,  $F_3$ , and  $F_4$  values were either taken from our previous work [18] or calculated from  $n$  and  $D$  literature data [19]. For all solvents, the  $\bar{\nu}_A$  values corresponding to the 260–300 nm region for BTBT, BTT, and MeOBTT, and to the 310–340 nm region for BTI were utilized; in Table I, they are indicated in boldface. The  $\bar{\nu}_F$  values of the long-wavelength fluorescence emission maxima (330–375 nm) were chosen for all fused benzothiophene derivatives. The results of the statistical treatment of the McRae, Suppan, and Kowski-Chamma-Viallet correlations are satisfactory (Table II). Indeed, as can be seen, a good linearity was found for the three types of relationships, with correlation coefficients larger than 0.90. Taking into account the experimental errors of about  $\pm 40 \text{ cm}^{-1}$  of absorption and fluorescence wave numbers, the standard deviations of the correlation slopes can be considered acceptable (Fig. 5). The correlations are obeyed by at least seven solvents for all compounds (Table II). All correlations slopes exhibit positive values, ranging from about 280 to  $1330 \text{ cm}^{-1}$ , which indicates the existence of a weak negative solvatochromism. Therefore, the excited singlet state dipole moment

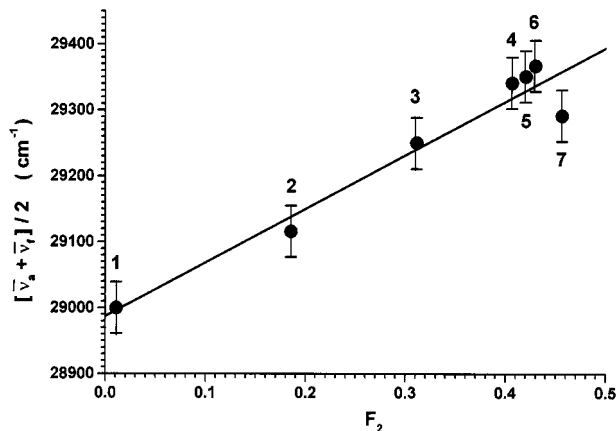


Fig. 5. Example of Kowski-Chamma-Viallet solvatochromic plot for BTI. Solvents: 1 = carbon tetrachloride; 2 = chloroform; 3 = dichloroethane; 4 = ethanol; 5 = acetonitrile; 6 = water; 7 = dimethylsulfoxide. Wave numbers are given with an experimental error of  $\pm 40 \text{ cm}^{-1}$ .

( $\mu_e$ ) of the fused benzothiophene derivatives under study should be slightly smaller than their ground-state counterparts ( $\mu_g$ ). It allows us to predict that these fused benzothiophenes are less polar in the excited singlet state than in the ground state.

#### Kamlet-Abboud-Taft Multiparameter Solvation Energy Relationships

To determine the respective contributions of the solvent polarity/polarisability, hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) abilities to the ground and singlet excited states solute-solvent interactions, we applied the Kamlet-Abboud-Taft multiparameter solvation relationship [20] to our electronic absorption and fluorescence spectra data and to fluorescence quantum yields:

$$(XYZ) = (XYZ)_0 + s\pi^* + a\alpha + b\beta \quad (4)$$

where  $(XYZ)$  is a solvatochromic property,  $\pi^*$  is the solvent polarity/polarizability,  $\alpha$  and  $\beta$  are the solvent HBD and HBA abilities, and  $s$ ,  $a$ , and  $b$  are the corresponding regression coefficients.

For the calculations, we applied the method of multiple linear regression analysis, which is known to give results comparable to those with the stepwise method, and we utilized  $\pi^*$ ,  $\alpha$ , and  $\beta$  parameter literature values [20].

The statistical results of the Kamlet-Abboud-Taft correlations, relative to absorption wave numbers, fluorescence wave numbers, and fluorescence quantum yields are summarized in Table III. In the case of  $\bar{\nu}_A$  or  $\bar{\nu}_F$ , the relationships exhibit a rather good linearity, as shown by the correlation coefficients larger than 0.90 (Fig. 6 and

Table II. Statistical Treatment of the Solvatochromic Correlations

Compound	Slope ( $\text{cm}^{-1}$ )	Intercept ( $\text{cm}^{-1}$ )	$r^a$	$n^b$
<i>Mac Rae Eq.</i>				
BTBT	$277 \pm 42$	32222	0.936	8
BTT	$393 \pm 77$	33823	0.901	8
BTI	$391 \pm 55$	30995	0.945	8
MeOBTT	$456 \pm 48$	35907	0.968	8
<i>Suppan Eq.</i>				
BTBT	$684 \pm 122$	32064	0.917	8
BTT	$1001 \pm 186$	33576	0.910	8
BTI	$968 \pm 170$	30772	0.918	8
MeOBTT	$1166 \pm 144$	35516	0.969	8
<i>Kowski-Chamma-Vialeq eq.</i>				
BTBT	$884 \pm 154$	30150	0.931	7
BTT	$1329 \pm 123$	32366	0.975	8
BTI	$815 \pm 93$	28987	0.969	7
MeOBTT	$749 \pm 141$	32788	0.940	7

<sup>a</sup>  $r$ : Correlation coefficient.

<sup>b</sup>  $n$ : number of solvents.

**Table III.** Statistical Treatment of the Kamlet-Abboud-Taft Solvation Energy Relationships for the Absorption and Fluorescence Spectral Data of Benzothiophenes

Compound	Spectral data	$s(\text{cm}^{-1})^a$	$a(\text{cm}^{-1})^b$	$b(\text{cm}^{-1})^c$	Intercept ( $\text{cm}^{-1}$ )	$r^d$	$n^e$
BTI	Absorption ( $\nu_a$ )	-249	-96	65	31645	0.939	9
	Fluorescence( $\nu_f$ )	157	-1	-26	30127	0.996	9
	Fluorescence quantum yield( $\phi_f$ ) <sup>f</sup>	-2	2	-3	3.26	0.839	6
BTBT	Absorption ( $\nu_a$ )	125	-105	51	37765	0.921	7
	Fluorescence( $\nu_f$ )	-68	237	310	28163	0.929	6
	Fluorescence quantum yield ( $\phi_f$ ) <sup>f</sup>	0.3	-0.4	1.66	6.83	0.901	7
BTT	Absorption ( $\nu_a$ )	223	-19	97	37037	0.910	7
	Fluorescence( $\nu_f$ )	-185	1946	342	30309	0.903	7
	Fluorescence quantum yield ( $\phi_f$ ) <sup>f</sup>	-1.21	0.61	-2.11	4.52	0.897	6
MeOBTT	Absorption ( $\nu_a$ )	1091	849	-126	36902	0.906	6
	Fluorescence( $\nu_f$ )	-172	133	-15	29411	0.912	6
	Fluorescence quantum yield ( $\phi_f$ ) <sup>f</sup>	-4	1	-1	7.93	0.925	5

<sup>a</sup>  $s$ : Polarity/polarizability coefficient [see Eq. (4)].

<sup>b</sup>  $a$ : HBD ability coefficient [see Eq. (4)].

<sup>c</sup>  $b$ : HBA ability coefficient [see Eq. (4)].

<sup>d</sup>  $r$ : Correlation coefficient.

<sup>e</sup>  $n$ : Number of solvents.

<sup>f</sup> In the case of fluorescence quantum yields, the solvation energy relationship obeys the following equation:  $\ln(1/\phi_f - 1) = s\pi^* + a\alpha + b\beta$

Table III). The majority of the solvents obeyed the correlations.

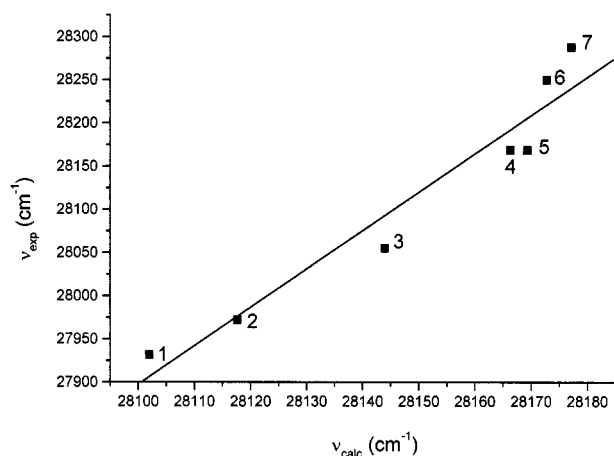
To the exception of BTI, the  $s$  coefficients present positive values for absorption spectral data, which indicates that increasing the solvent polarity/polarisability ( $\pi^*$ ) produces a blue-shift in  $\bar{\nu}_A$ . This shows that the ground state of benzothiophene derivatives becomes more stabilized when the solvent polarity increases, which seems in agreement with a negative solvatochromism.

In contrast, the  $s$  coefficients exhibit weakly negative values for fluorescence spectral data, except again in the

case of BTI. This shows that a bathochromic shift of  $\bar{\nu}_F$  occurs upon increasing the solvent polarity/polarisability ( $\pi^*$ ). This particular behavior seems to show that the excited singlet state of benzothiophene derivatives (except BTI) becomes slightly more stabilized when the solvent polarity increases.

The signs of  $a$  and  $b$  coefficients, obtained for absorption and fluorescence wave numbers, vary from one compound to another, and, in most cases, they present weaker values than  $s$  coefficients, which indicates that the ability of the solvent to donate or accept hydrogen bonds is weaker than the solute-solvent dipole-dipole interactions occurring in the ground and excited singlet states of most benzothiophene derivatives. A similar behavior was found in the case of a series of benzo[a]phenothiazines [21].

For the correlations of the fluorescence quantum yields, we used the approach of Burget and Jacques [22], who established a good relationship between  $\ln(1/\phi_F - 1)$  and the Kamlet-Abboud-Taft solvatochromic parameters in the case of the solvent effects on the thioxanthone fluorescence. When applying this equation to the benzothiophene derivatives, we obtained correlation coefficient values larger than 0.90, except in the case of BTI. As can be seen, the  $s$  and  $b$  coefficients generally present negative values (see Table III), which indicates a quantitative increase of the fluorescence quantum yield of benzothiophene derivatives with the solvent polarity/polarizability and hydrogen-bond acceptor ability. We observed recently analogous results in the case of the



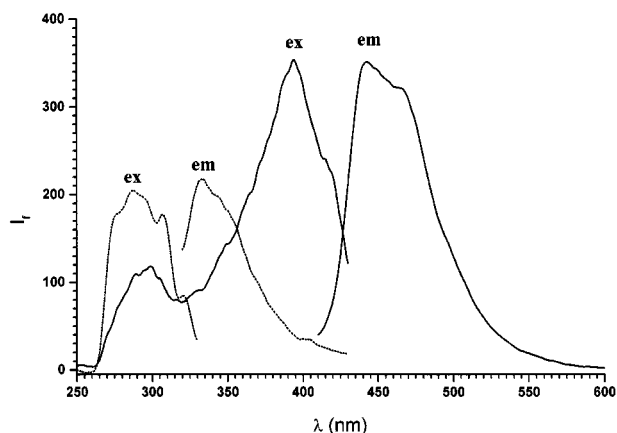
**Fig. 6.** Example of Kamlet-Abboud-Taft solvation energy relationship for the absorption spectral data of BTBT. Solvents: 1 = carbon tetrachloride; 2 = chloroform; 3 = toluene; 4 = dioxane; 5 = dichloroethane; 6 = ethyl acetate; 7 = acetonitrile.

solvent effect on the fluorescence quantum yields of poly(3-methoxythiophene) a conducting oligomer [9].

### Fluorescence Spectral Characteristics of Fused Benzothiophene Oligomers

In the course of an investigation on the electro-synthesis and characterization of poly(BTT) and poly(MeOBTT) [13], we found that the fluorescence spectral properties of these fused benzothiophene oligomers underwent dramatic changes relative to the parent monomers.

The fluorescence excitation spectra of  $2 \times 10^{-6}$  repeat unit (r.u.)  $L^{-1}$  poly(BTT) and poly(MeOBTT) solutions in dimethyl formamide display a wide, well-structured band with maxima at about 335 nm and 395 nm, respectively. These excitation maxima are strongly red-shifted by about 50 and 108 nm, respectively, against the BTT and MeOBTT excitation spectra recorded in the same conditions. On the other hand, the fluorescence emission spectra of the same solution of poly(BTT) and poly(MeOBTT) are characterized by a relatively wide, poorly structured band, centered at 410 nm and 445 nm, respectively (Fig. 7). These emission maxima also present dramatic red-shifts relative to the emission spectra of the parent monomers [ $\Delta\lambda_{em} = 80$  nm and 110 nm for poly(BTT) and poly(MeOBTT), respectively]. Moreover, a strong increase in the poly(BTT) and poly(MeOBTT) relative fluorescence intensity is also observed compared to that of the corresponding monomers. All these spectral features suggest that a significant  $\pi$ -electronic delocalization takes place in the excited singlet state of poly(BTT) and poly(MeOBTT), indicating the existence of important



**Fig. 7.** Excitation (ex) and emission (em) fluorescence spectra of  $2 \times 10^{-6}$  M MeOBTT (.....) and  $2 \times 10^{-6}$  r.u. $L^{-1}$  poly(MeOBTT) (solid curve) in dimethyl formamide.  $\lambda_{ex}$  and  $\lambda_{em}$  were 287 and 335 nm for MeOBTT and 395 and 445 nm for poly(MeOBTT).

conjugated segments in the oligomer chains. As already mentioned, we also demonstrated recently the occurrence of an extended conjugation in the PMOT hexamer singlet excited state, on the basis of a strong red-shift of the PMOT emission peak and a dramatic enhancement of the fluorescence intensity relative to the monomer [10].

### CONCLUSION

In this work we have investigated the structure and solvent effects upon the electronic absorption and fluorescence spectra and fluorescence quantum yields of four fused benzothiophene derivatives. Our study demonstrates the existence of a weak negative solvatochromism and a significant increase of the fluorescence quantum yields upon increasing solvent polarity, for all benzothiophenes. The satisfactory application of McRae, Suppan, and Kowski-Chamma-Viallet correlations to our spectroscopic results allows us to predict that the dipole moments of the fused benzothiophene derivatives should be slightly smaller in the excited singlet state than in the ground state. Moreover, the use of Kamlet-Abboud-Taft multiparameter solvation relationships indicates that, for most compounds, the solute-solvent dipole-dipole interactions are generally stronger than the ability of solvents to donate or accept hydrogen bonds. Our study of the fluorescence excitation and emission spectra of the electrogenerated fused benzothiophene oligomers [poly(BTT) and poly(MeOBTT)] shows the existence of dramatic red-shifts of the fluorescence maxima and important increases of the fluorescence intensity relative to the parent monomers. These results suggest the existence of extended electronic conjugation in the oligomer chains.

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