Luminescence Properties of Poly(3-Methoxythiophene)–Bithiophene Composite Oligomers

M. Fall,[1] J.-J. Aaron,[2,3] and D. Gningue-Sall[1]

The electronic absorption and fluorescence spectra of electrosynthesized poly(3-methoxythiophene)–bithiophene (PMOT-BT) composite oligomers were studied in organic solution (DMSO) and/or in the solid state on ITO plates. Different spectral properties (absorption and fluorescence maximum wavelengths, fluorescence quantum yields, etc.) were found to depend on the bithiophene initial concentration used during electrosynthesis and, subsequently, on the film composition and oligomer chain length.

INTRODUCTION

Luminescence spectroscopy has been widely applied in the past few years to study the microstructure, redox processes, and energy transfer in electrosynthesized or chemically prepared oligomers and polymers [1–8]. Recently, oligothiophene derivatives have been a subject of great interest because of their good chemical stability, electrical properties (in the doped state), and important use in optical applications, charge storage, and molecular electronics. However, until now, there is limited information concerning their luminescence properties [6–9].

Previously, we have investigated the electrosynthesis of poly(3-methoxythiophene) (PMOT) in an aqueous anionic micellar medium, using sodium dodecyl sulfate (SDS) as surfactant [5,10]. The optical and photophysical properties of the resulting films, constituted mainly of hexamers, were also studied [8,9]. Very recently, we performed the electrosynthesis of PMOT, using the same micellar medium in the presence of a small amount of bithiophene (BT) (10^{-3} M) [11]. We found that BT had an electrocatalytic effect on the MOT electrooxidation, allowing the electrodeposition of PMOT–BT composite films on Pt and Fe substrates [11].

In the present paper, we report on the influence of the initial bithiophene concentration on PMOT–BT optical and fluorescence properties. The structures of the oligomers under study are shown in Scheme I.

EXPERIMENTAL

All films were electrosynthesized potentiostatically (current density: $i=1$ mA/cm^2 during 5 min) on a Pt electrode as described previously [11]. PMOT was obtained from a H$_2$O–BuOH (96/4, v/v) solution containing 0.1 M MOT + 0.1 M SDS + 0.1 M LiClO$_4$. For PMOT–BT electrosynthesis, we added 10^{-3}, $5 \cdot 10^{-3}$, or $2 \cdot 10^{-2}$ M BT in H$_2$O–BuOH (94/6, v/v). PBT films were obtained using 0.05 M BT + 0.1 M SDS + 0.1 M LiClO$_4$ in H$_2$O–BuOH (90/10, v/v); the BuOH percentage was increased to solubilize the BT in the micellar medium.

The electronic absorption spectra were determined at room temperature (298 K) on a Perkin–Elmer UV–Vis Lambda 2 spectrometer. The fluorescence spectra were

[1] Département de Chimie, Faculté des Sciences et Techniques, Université C.A.D. de Dakar, Dakar, Sénégal.
[2] Institut de Topologie et de Dynamique des Systèmes de l'Université Paris 7—Denis Diderot, associé au CNRS–UPRESA 7086, 1 rue Guy de la Brosse, F-75005 Paris, France.
[3] To whom correspondence should be addressed.
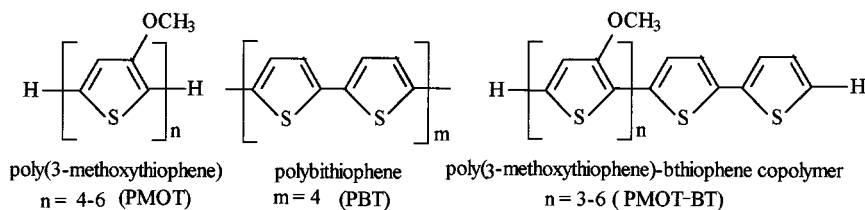
Scheme I. Structure of the oligomers under study.

recorded at 298 K using a Perkin–Elmer LS-50 spectro-photofluorometer.

The matrix-assisted light desorption-ionization, time of flight (MALDI-TOF) mass spectra of the films were obtained on a Voyager Elite (PerSeptive Biosystems, Framington, MA) Time of Flight mass spectrometer.

RESULTS AND DISCUSSION

Composition of the PMOT–BT Films

Before studying the electronic absorption and fluorescence spectra of the PMOT–BT films, we investigated their composition, using MALDI-TOF mass spectrometry [5]. The distribution of the oligomers in PMOT-BT films is shown in Table I. Upon adding small quantities of BT in the bulk electrolytic solution, composite films, including various amounts of PMOT (tetramers, pentamers, and hexamers), copolymers (with MOT and BT units), and tetra(bithiophene), are formed. As can be seen, an increase in the BT initial concentration from 10^{-3} to $2 \cdot 10^{-2}$ M provokes a significant increase of the copolymer percentage in the films.

Electronic Absorption Spectra

The electronic absorption spectral properties of the PMOT–BT films in their neutral form were recorded in

DMSO solution (Fig. 1) and in the solid state, on ITO sheets (Fig. 2), and compared with those of PMOT and PBT.

The PMOT–BT spectra are characterized by a main band in the 490- to 510-nm region, assigned to the delocalized $\pi \to \pi^*$ electronic transition and corresponding to the conjugated segments in the oligomer chain [12], and a secondary band in the 320- to 350-nm region. Upon going from film to DMSO solution, the main peaks show only rather small spectral shifts ($\Delta\lambda = 2$–18 nm) and molar absorption coefficient weak differences, which indicates a moderate change of the organization of the PMOT–BT oligomers in the solid state and in the solution.

However, two distinct spectral behaviors are apparent in both media. Indeed, in DMSO solution, the PMOT–BT main peaks (496–507 nm) are moderately red-shifted ($\Delta\lambda = 2$–9 nm) against PMOT and strongly red-shifted ($\Delta\lambda = 55$–66 nm) relative to the PBT maximum (441 nm). It is well known that the absorption band position of oligothiophenes depends on their chain length [13]. Since the PMOT–BT films are not only constituted of a mixture of PMOT and PBT, but also include copolymers of bithiophene and 3-methoxythiophene (Table I), the observed, weak red shift relative to PMOT can be attributed to the overall lengthening of the PMOT–BT chains by one bithiophene unit.. On the other hand, the strong red shift of the PMOT–BT absorption band against PBT is probably due to the methoxy group electrodonating

Table I. Composition of the PMOT–BT Films Prepared Using Different BT Initial Concentrations

[BT] (M)	(MOT)$_3$ BT	(MOT)$_4$ BT	(MOT)$_5$ BT	(MOT)$_6$ BT	(BT)$_4$	PMOT[a] (%)	PMOT–BT[b] (%)
0	—	—	—	—	—	100	0
10^{-3}	12.1	9.5	—	—	—	78.4	21.6
$5 \cdot 10^{-3}$	6.1	23.6	12.2	4.3	3.3	50.5	46.2
$2 \cdot 10^{-2}$	8.9	32.3	19.7	6.4	3.7	29.0	67.3

[a] Sum of the tetramer, pentamer, and hexamer percentages in the film.
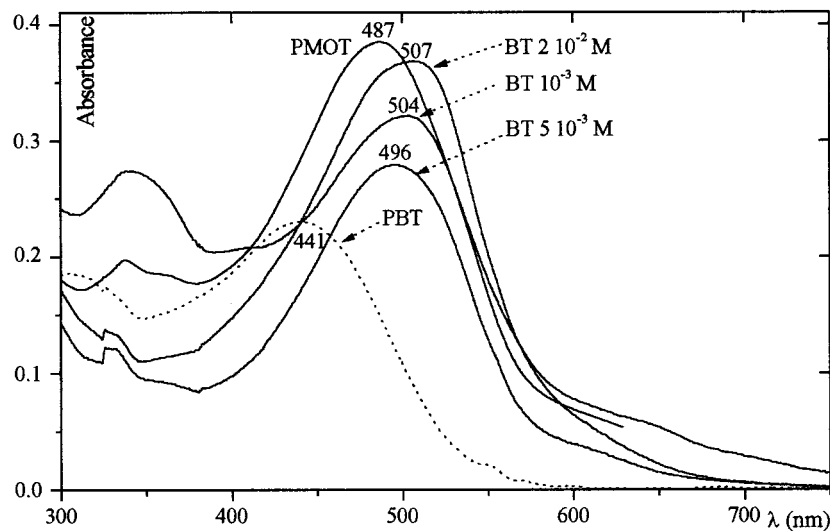[b] Total of the percentages of the various PMOT–BT copolymers.

Fig. 1. Electronic absorption spectra of 10^{-4} (r.u.) L^{-1} PMOT, PMOT–BT, and PBT DMSO solutions.

mesomer effect, producing a marked electronic delocalization in the oligothiophene chain [8,14].

In contrast, on ITO plates, the main maxima of the PMOT–BT of various compositions are significantly blue-shifted ($\Delta\lambda$ = 27–40 nm) against PMOT, which indicates a specific molecular orientation of PMOT–BT chains in the solid state, due to interactions between the oligomer molecules themselves. These spectral results suggest the existence of aggregation, which is more likely to occur in unsubstituted polybithiophene than in the (substituted) PMOT. A similar behavior has been observed recently in the case of the optical properties of oligothiophene and oligophenylvinylene nanoaggregates [4].
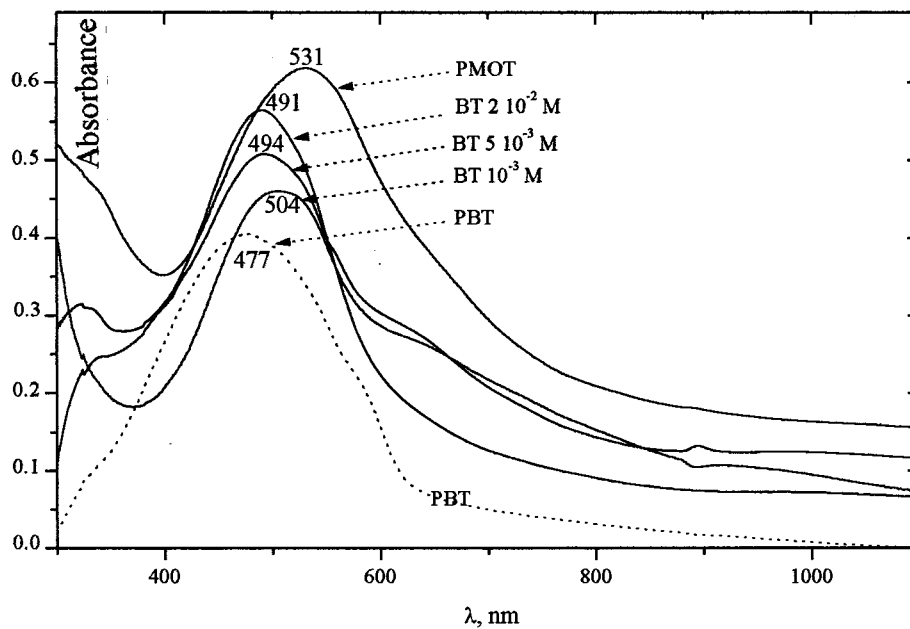

Fig. 2. Electronic absorption spectra of PMOT, PMOT–BT, and PBT neutral films on ITO.

Table II. Fluorescence Properties of PMOT, PMOT–BT, and PBT DMSO Solutions[a]

Compound	Copolymer (%)[b]	λ_{ex} (nm)	λ_{em} (nm)	ϕ_F[c]	τ_F[d]	τ_F component (%)[e]
PMOT	0	465	565	0.38	0.90	100
PMOT–BT1[f]	21.6	464	563	0.20	0.61	76
					2.13	24
PMOT–BT2[g]	46.2	466	562	0.28	—	—
PMOT–BT3[h]	67.3	466	559	0.23	0.81	88
					1.65	12
PBT	0	448	546	0.22	0.80	89
					2.53	11

[a] Concentration: 10^{-5} repeat unit (r.u.) L^{-1}, except for PBT, which was only partially soluble in DMSO.
[b] Total of the percentages of the various PMOT–BT copolymers.
[c] Fluorescence quantum yields evaluated against fluorescein as the standard ($\phi_F = 0.90$ at $25 \pm 5°C$) [15], on an SLM Aminco Bowman Series 2 luminescence spectrometer.
[d] Fluorescence lifetimes, measured as described previously on a laboratory-made multifrequency phase fluorimeter [8].
[e] Percentage of each exponential fluorescence decay.
[f] Electrosynthesized in the presence of $10^{-3} M$ BT.
[g] Electrosynthesized in the presence of $5 \times 10^{-3} M$ BT.
[h] Electrosynthesized in the presence of $2 \cdot 10^{-2} M$ BT.

Fluorescence Spectral Properties

We have investigated the fluorescence spectral properties of PMOT, PMOT–BT, and PBT neutral films in DMSO solution. Our results are summarized in Table II.

We found that the fluorescence emission spectra of PMOT and PBT in solution are strongly red-shifted against the corresponding monomers, respectively, MOT ($\Delta\lambda_{em} = 170$ nm) and BT ($\Delta\lambda_{em} = 150$ nm). A very large increase in the PMOT and PBT fluorescence intensity is also observed relative to the corresponding monomers, which confirms that extended π-conjugated electronic systems are involved in the PMOT and PBT oligomer chains.

On the other hand, the fluorescence excitation spectra of PMOT and PMOT–BT present a wide band centered at about 464–466 nm, which is moderately blue-shifted relative to the main absorption band maximum of these oligomers; this indicates that the excited species-
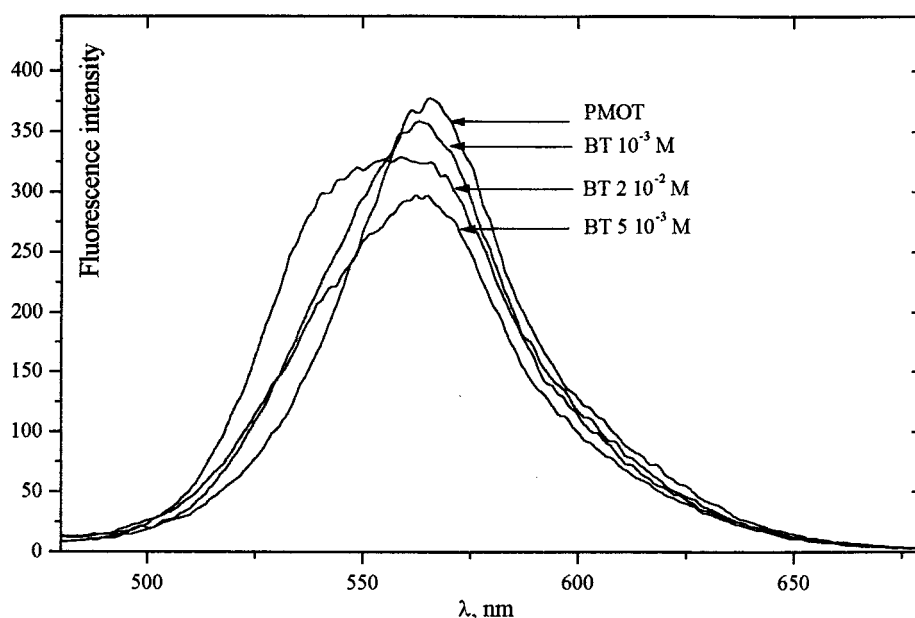

Fig. 3. Fluorescence emission spectra of 10^{-5} (r.u.) L^{-1} PMOT and PMOT–BT in DMSO solutions.

correspond to the absorbing species (see Table II and Fig. 1). The PMOT–BT emission spectra exhibit a broad, structureless peak located in the 559- to 563-nm region, which is weakly blue-shifted ($\Delta\lambda$ = 2–6 nm) against PMOT when the initial BT concentration increases from 0 to 2×10^{-2} M in the electrolytic medium of film preparation (Fig. 3). This fluorescence blue shift seems to vary simultaneously with the content of BT, which can be attributed to a higher aggregation occurring in the presence of this unsubstituted oligomer. Also, it is note worthy that the fluorescence quantum yields of PMOT–BT (ϕ_F = 0.20–0.28 in DMSO) decrease significantly relative to that of PMOT (ϕ_F = 0.38), which is ascribed to the presence of BT units within the oligomer chains (Table II). This result may be related to the PBT fluorescence quantum yield, much lower than that of PMOT. Finally, the fluorescence decay presents a markedly different behavior for PMOT and PMOT–BT. Indeed, the fluorescence lifetimes (τ_F) are monoexponential (τ_F = 0.90 ns) in the case of PMOT, whereas they present two exponential decays including a short-duration (τ_F = 0.61–0.81 ns) and a long-duration (τ_F = 1.65–2.13 ns) component for PMOT–BT and also for PBT (τ_F = 0.80 and 2.53 ns). All these features suggest the usefulness of fluorescence spectroscopy to gain information on the oligomer distribution in a composite film.

CONCLUSION

In this work, we have studied the luminescence properties of 3-methoxythiophene–bithiophene composite oligomers, electrogenerated using different bithiophene concentrations in the electrosynthesis medium. We have essentially shown the existence of parallel changes of the copolymer total percentages in the films, on the one hand, and of the absorption and luminescence properties (maximum absorption and fluorescence emission wavelengths, fluorescence quantum yields, fluorescence lifetimes), on the other hand. This demonstrates the possible application of electronic absorption and luminescence spectroscopy for investigating the chain lengths and oligomer distribution in copolymers films.

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