

Spectral characteristics of bithiophenes and terthiophenes linked with heterocyclic unit in solution and polymer matrix

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Abstract

Spectral characteristics of derivatives of thiophene substituted on heteroaromatic cycle as pyrazine was compared with terthiophene linked with cyano and hydrazo groups. The absorption, fluorescence and its lifetime were measured in solution (methanol, cyclohexane) and in polymer matrices (polystyrene, PS; polymethyl methacrylate, PMMA; and polyvinyl chloride, PVC). Derivatives with two thiophene units substitute on pyrazine exhibit the lowest wavenumber band in the region 26,320–25,600 cm⁻¹ and log ϵ ~4.0, which is not influenced by the medium. Derivatives with benzene and pyridine ring annealed to pyrazine (2,3-bis-(2'-thienyl)quinoxaline (I), 2,3-bis-(2'-thienyl)pyrido[2,3-b]pyrazine (III)) exhibit fluorescence in polar methanol with maximum at 22,200 cm⁻¹ and quantum yield of about 0.2 which is blue-shifted in going to non-polar solvent. The maximum fluorescence is slightly blue-shifted in polymer matrices as compared to methanol. Derivatives with annealed thiophene to pyrazine or substituted with two cyano groups (2,3-bis-(2'-thienyl)thieno[3,4-b]pyrazine (II), 2,3-dicyano-5,6-bis(2'-thienyl)pyrazine (IV)) do not yield any emission. Derivatives with terthiophene structural units ([2,2',5',2'']-terthiophene-[2]-thienylacrylonitrile (V) [2,2',5',2'']-terthiophene-5-carbaldehydehydrazone (VI)) exhibit fluorescence with maximum around 20,000 cm⁻¹. The lifetime of fluorescence of all thiophene was 1 ns or shorter. The polymer matrices increase the intensity of fluorescence to some extent and prolong the lifetime of thiophene derivatives. Derivative VI exhibits some tendency to an aggregation at higher concentration above 0.01 mol kg⁻¹ in polymer matrices. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiophenes; Terthiophenes; Pyrazines; Polymer matrices; Absorption; Fluorescence; Lifetime

1. Introduction

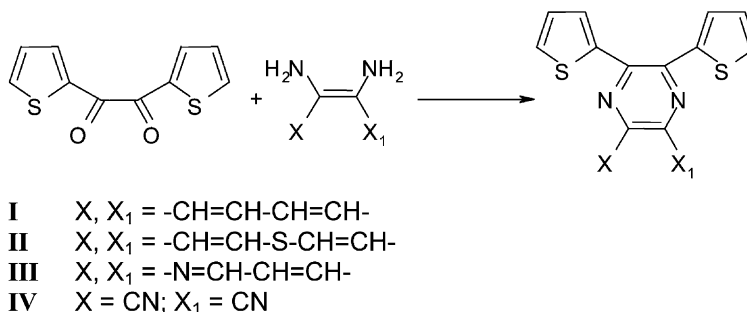
Conjugated organic polymers are of great interest because of their technical applications in molecular electronics, non-linear optics, as organic light emitting diodes, field effect transistors and sensors. In this respect, polythiophenes or its substituted derivatives are very promising materials [1,2]. Oligomers and polymers of substituted thiophenes have attracted much attention due to their conducting and spectral properties, and their processibility based on their solubility in common organic solvents. They have been subject of a number of photo-physical studies concerning the influence of microstructural changes of oligomers and polymers prepared in different way on their luminescent spectral properties [3–9]. The substitution of thiophene on the ring results in the increase in the solubility of oligomers and polymers in organic solvents and induces interesting phenomena such as solvatochromism and thermochromism [5,6]. Becker et al.

[3,4] found that the spectral properties of unsubstituted oligothiophene depend on the number of rings linked together. The increase of molar extinction coefficient, quantum yield of emission and lifetime was observed in going from bithiophene to oligomer with $n = 7$ due to less effective intersystem crossing (ISC) process in oligomers with longer chain.

The ISC process is determined by three factors: (1) the spin-orbit coupling factor, (2) the overlap which contains the energy difference of the corresponding singlet and triplet states in the denominator and the Franck-Condon integral, and (3) the density of original and terminal states. The main reasons for the effective ISC of oligothiophenes ($n = 2, 3$), determined by time resolved femto-second spectroscopy, are the high spin-orbit coupling factor due to sulphur and almost isoenergetic positions of S₁ and T₂ states determined by photo-detachment photoelectron spectroscopy [9].

In this paper, we report the spectral properties namely absorption, emission and lifetime of emission of two thiophene rings linked with the heterocyclic ring as pyrazine (Scheme 1, compounds I–IV). In one derivative, thiophene is a part of the heterocycle ring system (II) as well. In

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Scheme 1.

other two derivatives, terthiophene chromophores are linked with electron accepting cyano (**V**) or hydrazo group (**VI**). The spectral properties in non-polar and polar solutions are compared with those in polymer matrices. The aim of the study is to suggest the structural units based on thiophene with increased yield of radiation decay (quantum yield of emission) and prolonged lifetime in polymer matrices for application as organic light emitting diodes and exhibiting thermochromism or solvatochromism.

2. Experimental

The derivatives of thiophene **I–IV** (Scheme 1) have been prepared by the condensation of 2,2'-thienil (mp 81–82°C) [10] with *o*-diamines as 1,2-phenylenediamine (Aldrich, mp 103–105°C), 3,4-diaminothiophene (Across, mp 96–97°C), 2,3-diaminopyridine (Aldrich, mp 114–116°C), diaminomaleonitrile (DAMN) (Aldrich, mp 178–179°C), and employing the following general procedure. A 10 mmol solution of *o*-diamines in 100 ml of absolute ethanol was treated with 10 mmol of 2,2'-thienil and 1 ml of acetic acid and then heated under reflux for 4 h. The warm solution was neutralized with 1 N NaHCO₃ and the precipitate was collected after cooling. The crude product was obtained and purified by crystallization or separated on silica gel (Merck 60).

2.1. 2,3-Bis-(2'-thienyl)quinoxaline (**I**)

mp: 143–145°C (ethanol) (89% yield) [10–12]. ¹H NMR (DMSO-d₆, 300 MHz, ppm): 8.0 (m, 2H, H-C₆H₄, *J* = 8.8 Hz, *J* = 1.4 Hz), 7.79 (m, 2H, H-C₆H₄, *J* = 8.8 Hz, *J* = 6.6 Hz), 7.75 (dd, 2H, H-5,5', *J*_{5,4} = 5.2 Hz, *J*_{5,3} = 1.2 Hz), 7.17 (dd, 2H, H-3,3', *J*_{3,4} = 3.7 Hz, *J*_{3,5} = 1.2 Hz), 7.06 (dd, 2H, H-4,4', *J*_{4,5} = 5.1 Hz, *J*_{4,3} = 3.7 Hz). ¹³C NMR (CDCl₃, 75.47 MHz): 146.1, 140.8, 139.8, 130.6, 129.8, 129.4, 128.4, 127.8.

IR (KBr; ν cm⁻¹): 3111, 3093, 3068, 3056, 2924, 2850, 1637, 1522, 1423, 1133, 853, 761, 711. UV (methanol): λ_{max}, nm (log ε, dm³ mol⁻¹ cm⁻¹): 226 (4.34), 255 (4.50), 291 (4.39), 381 (4.26).

2.2. 2,3-Bis-(2'-thienyl)thieno[3,4-*b*]pyrazine (**II**)

mp: 183–185°C (70% yield). Anal. Calc. for C₁₄H₈N₂S₃ (300.41): C, 55.97; H, 2.68; S, 32.02. Found: C, 55.54; H, 2.57; S, 31.78. Mass (*M*⁺ 300, 80%): 267, 255, 217, 191, 150, 128, 111, 82 (100%), 71, 69, 64, 57, 45, 39. ¹H NMR (DMSO-d₆, 300 MHz, ppm): 8.33 (s, 2H, H-2,5), 7.77 (dd, 2H, H-5,5', *J*_{5,4} = 5.2 Hz, *J*_{5,3} = 1.2 Hz), 7.09 (dd, 2H, H-3,3', *J*_{3,4} = 3.7 Hz, *J*_{3,5} = 1.2 Hz), 7.06 (dd, 2H, H-4,4', *J*_{4,5} = 5.1 Hz, *J*_{4,3} = 3.7 Hz). ¹³C NMR (DMSO-d₆, 75.47 MHz, ppm): 145.79, 141.24, 140.06, 129.79, 129.62, 127.67, 118.54.

IR (KBr; ν cm⁻¹): 3108, 3085, 3071, 2923, 2854, 1638, 1541, 1429, 1422, 1278, 1080, 864, 765, 723, 707. UV (methanol): 269 (4.49), 388 (4.24).

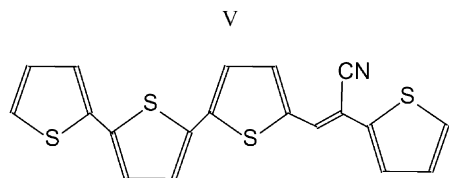
2.3. 2,3-Bis-(2'-thienyl)pyrido[2,3-*b*]pyrazine (**III**)

mp: 124–125°C (75% yield). Anal. Calc. for C₁₅H₉N₃S₂ (295.02): C, 60.99; H, 3.07; S, 21.71. Found: C, 60.79; H, 3.01; S, 21.51. Mass (*M*⁺ 295, 20%): 221, 185, 186, 111 (100%), 83, 71, 57, 45, 39. ¹H NMR (DMSO-d₆, 300 MHz, ppm): 9.08 (m, 1H), 8.44 (m, 2H), 7.80 (dd, 2H, H-5,5'), 7.29 (dd, 2H, H-4,4'), 7.11 (dd, 2H, H-3,3'). ¹³C NMR (DMSO-d₆, 75.47 MHz): 154.6, 148.6, 148.4, 146.9, 140.6, 140.1, 137.3, 135.1, 131.0, 130.3, 130.1, 129.9, 127.9, 127.8, 125.9.

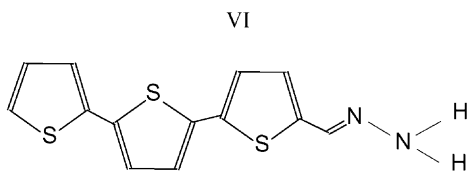
IR (KBr; ν cm⁻¹): 3095, 3073, 2963, 2926, 1718, 1636, 1442, 1418, 1232, 1183, 1044, 786, 715. UV (methanol): 259 (4.50), 308 (4.34), 392 (4.30).

2.4. 2,3-Dicyano-5,6-bis(2'-thienyl)pyrazine (**IV**)

mp: 180–182°C (ethanol), (87% yield). Anal. Calc. for C₁₄H₆N₄S₂ (294.23): C, 57.12; H, 2.05; S, 21.79. Found: C, 56.91; H, 1.94; S, 21.51. Mass (*M*⁺ 294, 90%), 261, 250, 249, 111, 110, 109 (100%), 93, 82, 70, 69, 64, 58, 45. ¹H NMR (DMSO-d₆, 300 MHz, ppm): 7.63 (dd, 2H, H-3,3', *J*_{3,4} = 3.7 Hz, *J*_{3,5} = 0.8 Hz), 7.66 (dd, 2H, H-5,5', *J*_{5,4} = 4.1 Hz, *J*_{5,3} = 0.8 Hz), 7.14 (t, 2H, H-4,4', *J*_{4,5} =



[2,2',5',2'']-terthiophene-[2]-thienylacrylonitrile (V).



[2,2',5',2'']-terthiophene-5-carbaldehydehydrazone (VI).

Scheme 2.

4.1 Hz, $J_{4,3} = 3.7$ Hz). ^{13}C NMR (CDCl_3 , 75.47 MHz): 147.9, 137.9, 133.1, 131.4, 128.5, 128.1, 113.0.

IR (KBr; $\nu \text{ cm}^{-1}$): 3118, 3100, 3086, 2242, 1637, 1509, 1500, 1419, 1370, 1076, 1059, 855, 846, 739, 728. UV (methanol): 219 (4.07), 254 (3.87), 326 (4.07), 382 (4.01).

The structures of derivatives with terthiophene structural units **V** and **VI** are given in Scheme 2.

2.5. [2,2',5',2'']-Terthiophene-[2]-thienylacrylonitrile (V)

A solution of [2,2',5',2'']-terthiophene-5-carbaldehyde (1 g, 3.61 mmol) in 500 ml dry ethanol was treated under reflux with 2-thiopheneacetonitrile (0.44 g, 3.61 mmol) and 2 ml 0.1 N sodium ethanolate in ethanol for 5 h. After cooling, the red precipitate was filtered and crystallized from ethanol. Yield: 0.99 g (72%); mp: 152–157°C. Anal. Calc. for $\text{C}_{19}\text{H}_{11}\text{NS}_4$ (381.56): C, 59.81; H, 2.91; N, 3.67; S, 33.61. Found: C, 59.64; H, 2.87; N, 3.52; S, 33.43. ^1H NMR (CDCl_3 , 300 MHz, ppm): 7.43, 7.15 (dd, 2H, C-H, C-H_{arom}, $J = 3.9$), 7.39–7.02 (m, 10H, C-H_{arom}). ^{13}C NMR (CDCl_3 , 75.47 MHz, ppm): 141.74, 138.96, 138.05, 136.18, 135.01, 133.88, 131.76, 128.33, 128.28, 128.05, 126.86, 125.93, 125.08, 124.66, 124.22, 123.87, 117.12, 102.28.

IR (KBr; $\nu \text{ cm}^{-1}$): 3130, 3110, 2210, 1579, 1441, 1068, 796. UV (methanol): 253 (4.19), 267 (4.11), 336 (3.98), 427 (4.63).

2.6. [2,2',5',2'']-Terthiophene-5-carbaldehydehydrazone (VI)

A solution of [2,2',5',2'']-terthiophene-5-carbaldehyde (1 g, 3.61 mmol) in dry ethanol (500 ml) was treated under reflux with hydrazine hydrate (0.15 g, 4.69 mmol) for 10 h. After cooling, the solvent was evaporated and solid product was crystallized from ethanol. Yield: 0.66 g (63%); mp: 272–274°C. Anal. Calc. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{S}_3$ (290.43):

C, 53.76; H, 3.47; N, 9.65; S, 33.12. Found: C, 53.52; H, 3.38; N, 9.48; S, 32.95. ^1H NMR (CDCl_3 , 300 MHz, ppm): 7.84 (s, 1H, CH=N), 7.23–6.93 (m, 7H, CH_{arom}), 5.50 (s, 2H, NH₂). ^{13}C NMR (CDCl_3 , 75.47 MHz) 138.98, 137.49, 137.28, 136.99, 136.59, 135.99, 127.91, 127.39, 124.69, 124.63, 124.43, 123.83, 123.44.

IR (KBr; $\nu \text{ cm}^{-1}$): 3300, 3050, 1605, 1466, 1448, 1080, 812, 725. UV (methanol): 246 (4.16), 311 (3.74), 387 (4.59).

All of the reagents used are commercially available and were used without further purification. ^1H and ^{13}C NMR spectra were recorded at 80 and 300 MHz, respectively, on a Tesla BS 487C and Varian VXR-300 NMR spectrometer, with chemical shifts referenced to TMS and to solvent residues (DMSO-d_6) and coupling constants calculated in Hertz. Mass spectra (EI) were measured with a GC-MS 25 RFA instrument (Kratos Analytical Manchester, UK), equipped with a direct inlet system at an ionization electron energy 70 eV, trap current of 100 mA at temperature of the ion source 200°C. IR spectra were measured on spectrometer PU 9800 FTIR and Impact 400 (Nicolet) in KBr pellets. The solvents methanol for UV (Slavus s.r.o., Bratislava), cyclohexane for UV (Merck, Darmstadt, Germany) were used. Anthracene (Lachema, Brno, ČR) used as the standard, was zonally refined. Quencher 1-oxo-2,2',6,6'-tetramethyl-4-hydroxypiperidine was the same as used previously [13].

Polymer films doped with the derivatives of thiophene were prepared by casting from solution. The following films were used as matrices: polystyrene (PS, Krasten, Kaučuk Kralupy a.s., CR, (SEC (chloroform) $M_n = 93,700$ $M_w/M_n = 2.7$)), polymethyl methacrylate (PMMA, Povazské Chemické Závody, a.s. Zilina, SR, $M_v = 1.01 \times 10^5$), polyvinyl chloride (PVC, Neralit 628, Spolana Neratovice, a.s., ČR $M_v = 1.11 \times 10^5$). Films were prepared by casting 0.02–2 mg of probe in 1 ml chloroform or tetrahydrofuran solution of polymer (5 g/100 ml) on a quartz or glass plate (28 mm \times 35 mm).

UV-VIS absorption spectra were recorded on a model M-40 spectrophotometer (C. Zeiss, Jena Germany). Emission spectra were recorded on a Perkin-Elmer MPF-4 spectrofluorimeter (Norfolk, CT, USA), which was connected through an interface and an ac-dc converter to a microcomputer for data collection, processing and plotting on an X-Y plotter [14]. The excitation wavelength was at the maximum of the longest wavelength band in the range 380–420 nm. Emission of solutions was measured in 1 cm cuvettes using a right-angle arrangement. The quantum yields for emission were determined relative to anthracene in methanol. Emission of polymer films was measured in a front-face arrangement using a Perkin-Elmer solid sample holder. The relative quantum yield for emission of each probe in each polymer film, was determined using anthracene as a standard doped in the same polymer. Polymer films were checked for the background emission, which was at least an order of magnitude lower in the most unfavorable case (low concentration of probe and high background emission).

Table 1
Spectral characteristics of 2,3-bis(2'-thienyl)quinoxaline (**I**)

Medium	$\nu_{\text{abs}}^{\text{a}}$ (cm ⁻¹)	$\log \epsilon^{\text{b}}$	$\nu_{\text{exc}}^{\text{c}}$ (cm ⁻¹)	$\nu_{\text{em}}^{\text{d}}$ (cm ⁻¹)	Φ^{e}	τ^{f}	$G^{1/2\text{g}}$	$\Delta\nu^{\text{h}}$ (cm ⁻¹)
MeOH	26250	4.26	25770	21980	0.17	0.12	1.2	4270
Cy	26180	3.87	26320	23310	0.10	0.10	1.0	2870
PS	25910	3.90	25970	22780	0.32	0.36, 0.16 ⁱ	1.9	3130
PMMA	26180	4.01	25770	22990	0.20	0.51, 0.67 ⁱ	1.7	3190
PVC	26180	3.88	25970	22830	0.18	0.51, 0.68 ⁱ	3.7	3350

^a Maximum of the lowest wavenumber absorption band.

^b Decadic molar extinction coefficient (dm³ mol⁻¹ cm⁻¹).

^c Excitation wavenumber.

^d Maximum of the fluorescence band.

^e Quantum yield of fluorescence relative to anthracene in methanol ($\phi = 0.21$).

^f Lifetime of fluorescence in solution at $c = 0.0001$ mol dm⁻³ and $c = 0.01$ mol kg⁻¹ in film evaluated according to [16,17].

^g S.E. of measurement according to [16].

^h Stoke's shift.

ⁱ Lifetime of fluorescence in film at 0.01 mol kg⁻¹ measured on LIF 200 connected to a PC, evaluated by program of J. Snyder, 1988 based on [17,18].

The relative quantum yields in film were determined according to the following relation [15]:

$$\Phi_{\text{F}} = \Phi_{\text{F}}^{\text{S}} \frac{\int_0^{\infty} I_{\text{F}}(\nu) d\nu}{\int_0^{\infty} I_{\text{F}}^{\text{S}}(\nu) d\nu} \left(\frac{1 - 10^{-A^{\text{S}}}}{1 - 10^{-A}} \right) \quad (1)$$

where $\Phi_{\text{F}}^{\text{S}}$ is the quantum yield of anthracene as a standard which was assumed to be 0.21 for all environments. For relative quantum yield, the value of $\Phi_{\text{F}}^{\text{S}}$ for anthracene was put at 1. Integrals $\int_0^{\infty} I_{\text{F}}(\nu) d\nu$ and $\int_0^{\infty} I_{\text{F}}^{\text{S}}(\nu) d\nu$ are the areas under the emission curve of the investigated compound and standard, and A and A^{S} are the absorbances of the investigated compound and standard, respectively.

Fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, Germany), which operates as a stroboscope. The excitation source was a nitrogen laser ($\lambda = 337$ nm) and emission was selected by cut-off filters. The output signal was digitized and transferred to a microcomputer [16]. Since the lifetime is short, deconvolution of instrument function from the measured decay was needed. Simple phase plane method was used, assuming that

Table 2
Absorption spectra of 2,3-bis(2'-thienyl)thieno[3,4-b]pyrazine (**II**)

Medium	$\nu_{\text{abs}}^{\text{a}}$ (cm ⁻¹)	$\log \epsilon^{\text{b}}$
MeOH	25770	4.24
Cy	25380	4.01
PS	25770	3.88
PMMA	25970	3.73
PVC	25770	3.98

^a Maximum of the lowest wavenumber absorption band.

^b Decadic molar extinction coefficient (dm³ mol⁻¹ cm⁻¹).

the decay is monoexponential [17,18]. The S.D. is given by $G^{1/2} = \sum((I_{\text{exp}} - I_{\text{calc}})^2/n)^{1/2}$, where I_{exp} and I_{calc} are the experimental and calculated intensities of emission, respectively. They were used to judge the quality of fit. It was assumed that decays were monoexponential if $G^{1/2} < 5\%$.

Static and time-resolved measurements were performed on the solution and the polymer films in the presence of air.

Relevant spectral data of derivatives **I–VI** in various media are given in Tables 1–6.

Table 3
Spectral characteristics of 2,3-bis(2'-thienyl)pyrido[3,4-b]pyrazine (**III**).

Medium	$\nu_{\text{abs}}^{\text{a}}$ (cm ⁻¹)	$\log \epsilon^{\text{b}}$	$\nu_{\text{exc}}^{\text{c}}$ (cm ⁻¹)	$\nu_{\text{em}}^{\text{d}}$ (cm ⁻¹)	Φ^{e}	τ^{f}	$G^{1/2\text{g}}$	$\Delta\nu^{\text{h}}$ (cm ⁻¹)
MeOH	25510	4.30	25320	25320	0.13			4590
Cy	25510	3.52						
PS	25320	3.95	25320	21790	0.17	0.3 ⁱ		3530
PMMA	25770	4.18	25320	21790	0.14	1.0, 0.7 ⁱ	5.3	3990
PVC	25380	4.15	25000	21100	0.17	0.8, 1.6 ⁱ	9.3	4280

^a Maximum of the lowest wavenumber absorption band.

^b Decadic molar extinction coefficient (dm³ mol⁻¹ cm⁻¹).

^c Excitation wavenumber.

^d Maximum of fluorescence band.

^e Quantum yield of fluorescence relative to anthracene in methanol ($\phi = 0.21$).

^f Lifetime of fluorescence in solution at $c = 0.0001$ mol dm⁻³ and $c = 0.01$ mol kg⁻¹ in film evaluated according to [16,17].

^g Standard error of measurement according to [16].

^h Stoke's shift.

ⁱ Lifetime of fluorescence in film at 0.01 mol kg⁻¹ measured on LIF 200 connected to PC, evaluated by software of J. Snyder 1988 based on [17,18].

Table 4
Absorption spectra of 2,3-dicyano-5,6-bis(2'-thienyl)pyrazine (**IV**)

Medium	$\nu_{\text{abs}}^{\text{a}}$ (cm^{-1})	$\log \epsilon^{\text{b}}$
MeOH	26180	4.01
Cy	26180	3.18
PS	233109	3.20
PMMA	23470	3.26
PVC	23700	3.48

^a Maximum of the lowest wavenumber absorption band.

^b Decadic molar extinction coefficient ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

3. Results and discussion

The absorption and fluorescence spectra were measured in non-polar and polar solvents (cyclohexane, methanol), which are solvents still dissolving the derivatives of thiophene. These compounds seem to be well compatible with polymer matrices at concentrations 0.001 and 0.01 mol kg⁻¹. The polarity of the used polymer matrices lies between the limits given by the used solvents. The dynamics of the solvent envelope in the low molecular solvent is substantially faster than in glassy polymer matrix. The shape of

absorption spectra of disubstituted thiophene derivatives on heterocyclic ring (pyrazine) for all derivatives (**I–III**) are quite similar (Fig. 1). The longest wavelength band in the region 26,300–25,600 cm⁻¹ is clearly distinct but it is rather broad expressed as FWHM equal 5200 cm⁻¹. The substitution of two cyano groups on the pyrazine ring decreases the absorption ability of **IV** (Fig. 1). For all the derivatives, **I–IV**, the molar extinction coefficient is lower in the non-polar solvent than in polar methanol. The values of the molar extinction coefficients in polymer films are loaded with higher error than in solution. They lie usually between the values determined in the solvents. In case of **IV**, the values of molar extinction coefficient are lower in polymer films than in methanol and similar as in cyclohexane (Table 4).

The absorption and fluorescence spectra of derivatives **I** and **III** in different media are shown in Figs. 2 and 3. The fluorescence of derivatives **I** and **III** is rather broad, structureless band and FWHM is 2300 cm⁻¹. The quantum yield of emission of both derivatives is around 0.2, which is comparable with anthracene (Tables 1 and 3). The fluorescence of **I** is red-shifted in going from cyclohexane to methanol where the largest Stoke's shift is around 4200 cm⁻¹ but in

Table 5
Spectral properties of [2,2',5',2'']-terthiophene-[2]-thienylacrylonitrile (**V**)

Medium	$\nu_{\text{abs}}^{\text{a}}$ (cm^{-1})	$\log \epsilon^{\text{b}}$	$\nu_{\text{exc}}^{\text{c}}$ (cm^{-1})	$\nu_{\text{em}}^{\text{d}}$ (cm^{-1})	ϕ^{e}	τ^{f} (ns)	$G^{1/2\text{g}}$	$\Delta\nu^{\text{h}}$ (cm^{-1})
MeOH	23420	4.63	25000	18830	0.05	1.0	7.5	4590
Cy	23920	4.37	23810	19760	0.04			4160
PS	22880	4.03	23810	18320	0.13	1.3, 1.2 ⁱ	6.9	4560
PMMA	22880	4.40	21320	18380	0.23	0.7, 0.5 ⁱ	2.8	4500
PVC	22320	4.41	22730	17760	0.12	0.5, 0.4 ⁱ	3.8	4560

^a Maximum of the lowest wavenumber absorption band.

^b Decadic molar extinction coefficient ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

^c Excitation wavenumber.

^d Maximum of the fluorescence band.

^e Quantum yield of fluorescence relative to anthracene in methanol ($\phi = 0.21$).

^f Lifetime of fluorescence in solution at $c = 0.0001 \text{ mol dm}^{-3}$ and $c = 0.01 \text{ mol kg}^{-1}$ in film evaluated according to [16].

^g Standard error of measurement according to [16].

^h Stoke's shift.

ⁱ Lifetime of fluorescence in film at 0.01 mol kg⁻¹ measured on LIF 200 connected to PC, evaluated by software of J. Snyder 1988 based on [17,18].

Table 6
Spectral properties of [2,2',5',2'']-terthiophene-5-carbaldehydehydrazone (**VI**)

Medium	$\nu_{\text{abs}}^{\text{a}}$ (cm^{-1})	$\log \epsilon^{\text{b}}$	$\nu_{\text{exc}}^{\text{c}}$ (cm^{-1})	$\nu_{\text{em}}^{\text{d}}$ (cm^{-1})	ϕ^{e}	τ^{f} (ns)	$G^{1/2\text{g}}$	$\Delta\nu^{\text{h}}$ (cm^{-1})
MeOH	25710	4.82	25000	19500	0.1	1.1	4.5	6210
Cy	26180	4.80	26320	21550, 21320	0.03	0.4	2.4	4860
PS	25510, 22520s	4.19, 4.04	25000	21140	0.21	0.5, 0.9 ⁱ	5.6	4370
PMMA	25380, 23700s	4.62	25060	21230	0.13	1.2, 0.7, 0.8 ⁱ	3.3, 5.0	4150
PVC	25190, 22220s	4.25	23810	21190	0.10	1.0 ⁱ		4000

^a Maximum of the lowest wavenumber absorption band; s mean shoulder.

^b Decadic molar extinction coefficient ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1\text{s}}$).

^c Excitation wavenumber.

^d Maximum of the fluorescence band.

^e Quantum yield of fluorescence relative to anthracene in methanol ($\phi = 0.21$).

^f Lifetime of fluorescence in solution at $c = 0.0001 \text{ mol dm}^{-3}$ and $c = 0.01 \text{ mol kg}^{-1}$ in film evaluated according to [16,17].

^g Standard error of measurement according to [16].

^h Stoke's shift.

ⁱ Lifetime of fluorescence in film at 0.01 mol kg⁻¹ measured on LIF 200 connected to PC, evaluated by program of J. Snyder 1988 based on [17,18].

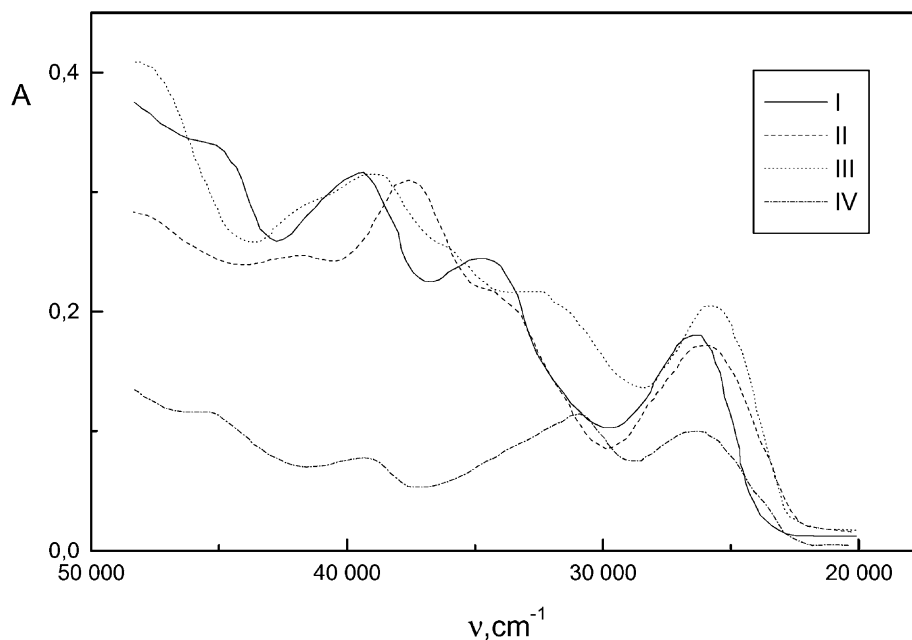


Fig. 1. Absorption spectra of derivatives of thiophene in methanol at 10^{-5} mol dm $^{-3}$ for **I** (solid line), **II** (dashed line), **III** (dotted line) and **IV** (dash dotted line).

most other media it is around 3000 cm^{-1} . In polymer matrices, maximum of the fluorescence lies between these limiting values. Derivative **III** does not yield measurable emission in cyclohexane, which might be due to the change of character of the lowest excited state of the fused pyridine ring. The lifetime of emission of **I** is around 0.1 ns in

solution, which is the limit of resolution of the used experimental set-up. In polymer matrices lifetime of fluorescence of **I** is rather longer. Although the values of lifetime are charged with large error, some prolongation of lifetime in polymer matrices is evident. The lifetime of **III**, around 1 ns, was determined in polymer matrices only. The absence of

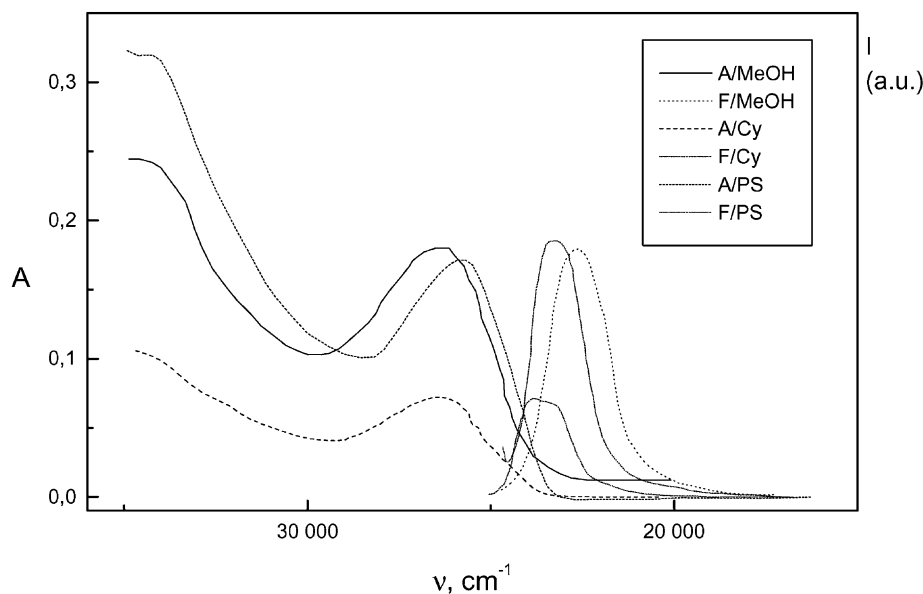


Fig. 2. Absorption (*A*) and fluorescence (*F*) spectra of **I** in methanol (MeOH) at 10^{-5} mol dm $^{-3}$ (*A* (solid line) and *F* (dotted line)), in cyclohexane (Cy) at 10^{-5} mol dm $^{-3}$ (*A* (dashed line), *F* (dash dotted line)) and in PS at 0.001 mol kg $^{-1}$ (*A* (short dashed line), *F* (short dotted line)). The fluorescence bands are normalized to the respective absorption bands.

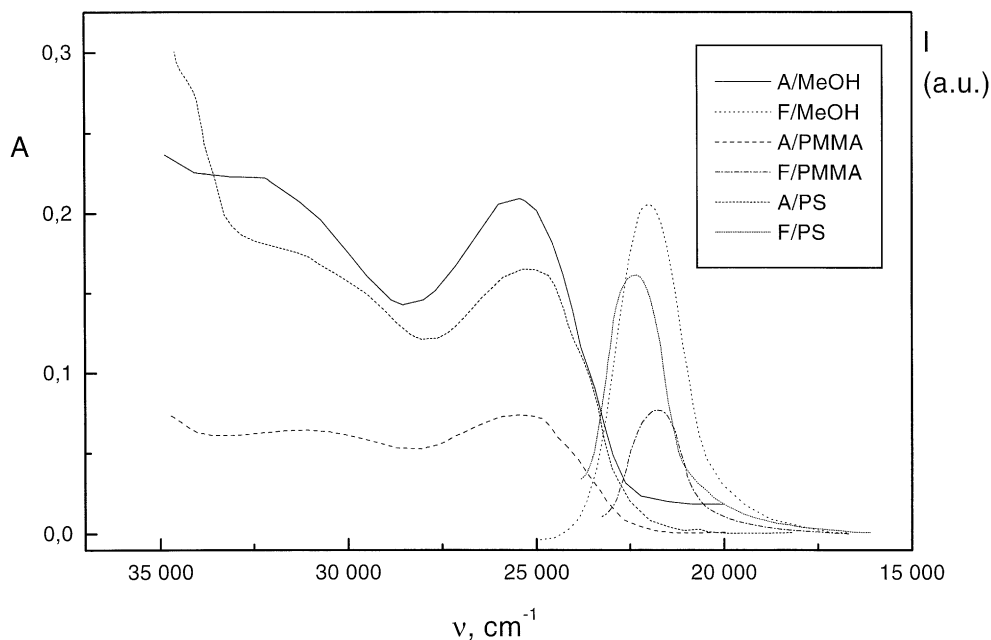


Fig. 3. Absorption (*A*) and fluorescence (*F*) spectra of **III** in methanol (MeOH) at 10^{-5} mol dm $^{-3}$ (*A* (solid line), *F* (dotted line)), PMMA at 0.001 mol kg $^{-1}$ (*A* (dashed line), *F* (dash dotted line)) and in PS at 0.001 mol kg $^{-1}$ (*A* (short dashed line), *F* (short dotted line)). The fluorescence bands are normalized to the respective absorption bands.

measurable emission of **II** and **IV** indicates that radiationless channel is more effective than the radiative one for these derivatives. In derivative **II**, the sulphur of the fused thiophene to pyrazine probably increases the intersystem crossing due to higher spin-orbit interaction [3]. In derivative **IV**, the two cyano groups could have similar effect.

Absorption and fluorescence spectra of derivatives **V** and **VI** are shown in Figs. 4 and 5. The absorption spectra of derivatives with terthiophene units **V** and **VI** are dominated by the intense lowest wavenumber band around 23,250 cm $^{-1}$ with FWHM = 5000 cm $^{-1}$ for **V**. It is hypsochromically shifted to 25,640 cm $^{-1}$ for **VI** as for pyrazine type

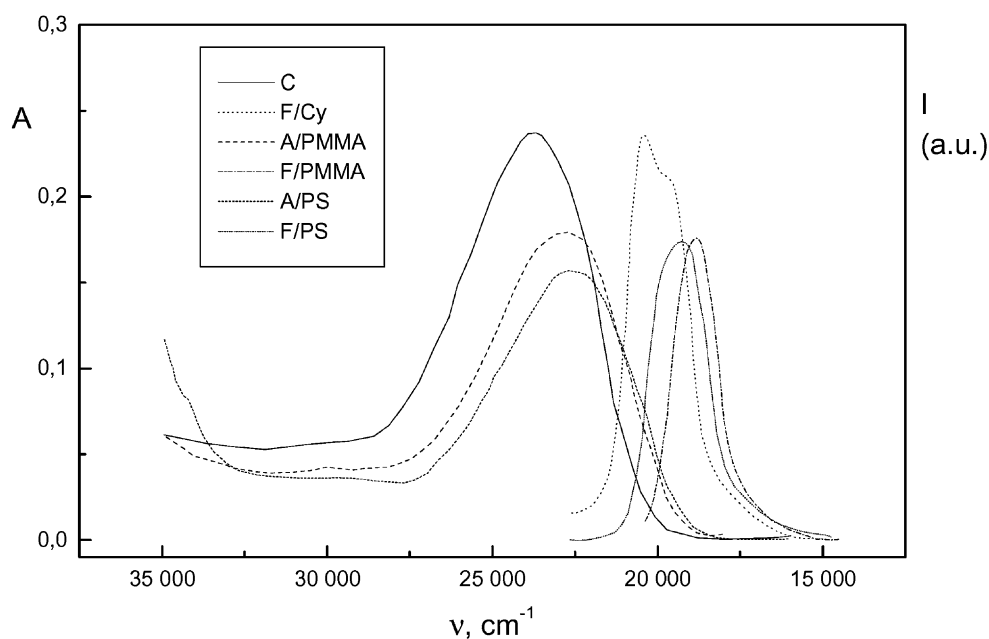


Fig. 4. Absorption (*A*) and fluorescence (*F*) spectra of **V** in cyclohexane (Cy) at 10^{-5} mol dm $^{-3}$ (*A* (solid line), *F* (dotted line)), PMMA at 0.001 mol kg $^{-1}$ (*A* (dashed line), *F* (dash dotted line)) and in PS at 0.001 mol kg $^{-1}$ (*A* (short dashed line), *F* (short dotted line)). The fluorescence bands are normalized to the respective absorption bands.

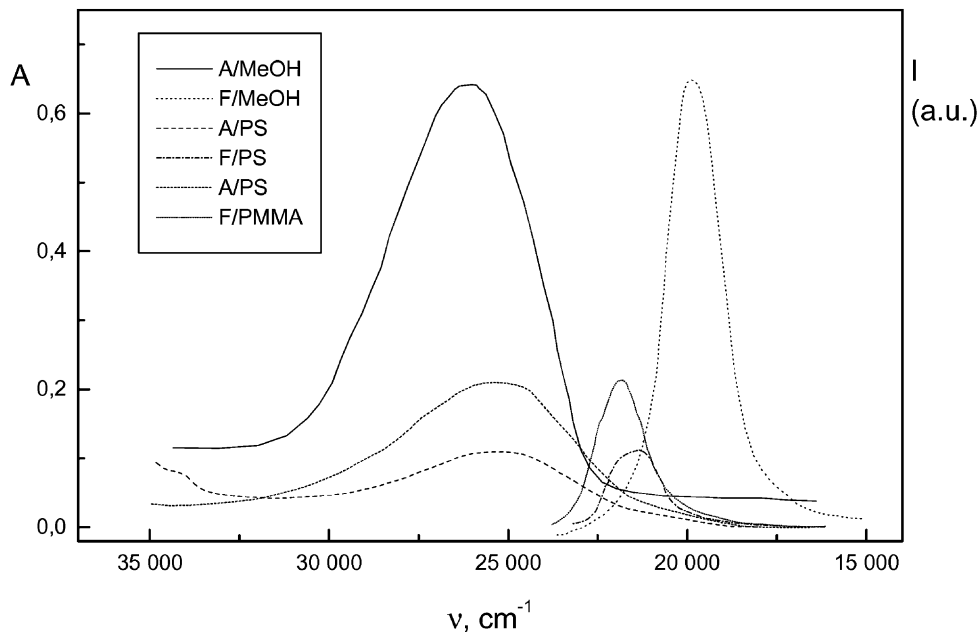


Fig. 5. Absorption (*A*) and fluorescence (*F*) spectra of **VI** in methanol (MeOH) at 10^{-5} mol dm $^{-3}$ (*A* (solid line), *F* (dotted line)), in PS at 0.001 mol kg $^{-1}$ (*A* (dashed line), *F* (dotted line)) and in PMMA at 0.001 mol kg $^{-1}$ (*A* (short dashed line), *F* (short dash dotted line)). The fluorescence bands are normalized to the respective absorption bands.

derivatives. The electron acceptor acrylonitrile with thiophene ring attached in **V** interacts more strongly with terthiophene chromophore than azine group, although both substituents extend the electronic system.

The main features of absorption spectra of derivatives under study in solution and in polymer matrices are nearly the same for all the derivatives **I–VI** (Figs. 2–5). At higher

concentration of all the derivatives under study in polymer matrices (0.01 mol kg $^{-1}$) there is slight extension of the edge of the lowest wavenumber band to red in the polymer matrices. This extension is clearly seen as a shoulder in Fig. 6 for **VI** in the PS matrix above $25,000$ cm $^{-1}$. Comparison of the shape of absorption band at lower concentration (0.001 mol kg $^{-1}$) with that at higher concentration

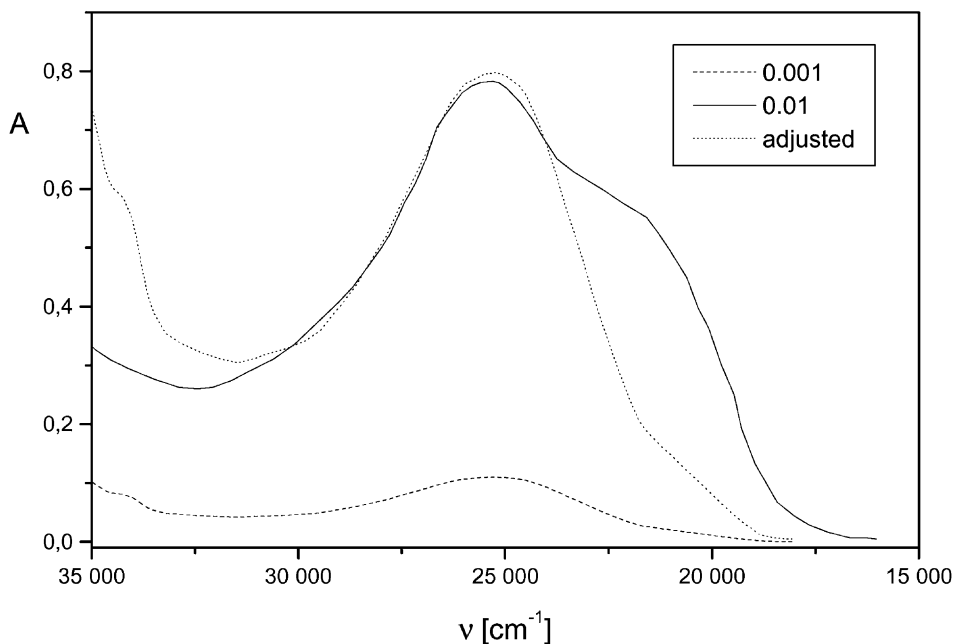


Fig. 6. Comparison of absorption spectrum of **VI** in PS matrix at 0.001 mol kg $^{-1}$ (dashed line) and at 0.01 mol kg $^{-1}$ (solid line). Dotted line is the absorption at lower concentration adjusted to the height of absorption at higher concentration.

(0.001 mol kg⁻¹) clearly shows that this extension of the absorption band is a concentration effect. The excitation spectra of **VI** in the polymer matrices exhibit the same features as the absorption spectra at lower and higher concentrations of dopant in polymer matrix namely shoulder at lower wavenumber side of the band. Maximum of the excitation spectrum of **VI** in all polymer matrices is red-shifted about 600 cm⁻¹ as compared to the absorption band. This might indicate some aggregation of these derivatives at higher concentration in polymer matrices. Clearly, **VI** exhibits a distinct aggregation in polymer matrices.

Derivative **V**, in which terthiophene chromophore is in conjugation with acrylonitrile group, yields fluorescence with maximum in the range 20,000–18,900 cm⁻¹ in solution and with low quantum yield 0.05 (Table 5). The fluorescence in all polymer matrices is red-shifted as compared with the solution showing some sign of shoulder at high wavenumber edge (Fig. 4). The quantum yield of fluorescence is higher around 0.1. The lifetime of fluorescence is around 1 ns. It was difficult to measure lifetime of **V** in cyclohexane due to the weak signal. It is shortened in polar polymer matrices (Table 5). The Stoke's shift is large about 4500 cm⁻¹ indicating that the geometry of ground and singlet excited states could be rather different.

Derivative **VI**, in which terthiophene chromophore are linked with azine group, exhibits fluorescence with maximum in the range 21,300–19,000 cm⁻¹ blue-shifted in comparison to **V** (Fig. 5). This fact indicates that singlet energy is higher and consequently the extent of conjugation in ground or excited states is lower than in **V**. The quantum yield of emission is comparable in polar methanol and in polymer matrices with anthracene; but substantially lower in non-polar cyclohexane. In cyclohexane, **VI** exhibits some shoulder at the high wavenumber side of the broad band while in other media only the broad band is observed. The lifetime of fluorescence of **VI** in most media is around 1 ns (Table 6). Although by linking of terthiophene chromophore with azido and 1-cyano-1-thiophenylethynyl groups, the electronic system is extended, no substantial increase is observed in the quantum yield and lifetime, which are parameters important for the application of these materials as organic light emitting diodes.

The fluorescence of these derivatives based on thiophene is effectively quenched by stable free radical 1-oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine indicating that singlet state of these derivatives is well above the one of quencher (Table 7). Since we know the lifetime of fluorescence, bimolecular rate constant of quenching can be calculated. The value of k_q is slightly higher for anthracene but substantially higher for derivative **I**. Although the lifetime determination is loaded with high error, the values of k_q are rather high above the bimolecular rate constant limited by diffusion. Reason for such effective quenching might either be the formation of ground state complex or some other mechanism connected with the presence of paramagnetic centre of the free radical.

Table 7

Quenching of thiophene derivatives **I–VI** by 1-oxo-2,2,6,6-tetramethyl-4-hydroxypiperidinom in methanol

Chromofores	K_{SV} (mol dm ³)	τ (ns)	$k_q \times 10^{10}$ (dm ³ mol ⁻¹ s ⁻¹)
Anthracene	268	4	6.7
I	155	0.1	155
II			
III	110	1.6	7.1
IV			
V	114	1.0	11.4
VI	81	1.1	7.4

In conclusion, the spectral data of the investigated derivatives show that linking of thiophene to heterocyclic pyrazine ring results in both increase as well as decrease in fluorescence, depending on the structure of the heterocyclic unit. The extension of terthiophene electronic system by substitution results in some improvement in the spectral properties. The doping of these derivatives in polymer matrices does not change the basic spectral features as compared in solution. In some cases, higher quantum yield and longer lifetime is observed for the derivatives (mainly **I**) doped in polymer matrix.

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