Novel fluorescence probe based on pyrene and piperazine; spectral properties in solution and in polymer matrices

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Abstract

New fluorescence probe, composed of pyrene and piperazine [15-(1-pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane] was prepared, spectrally characterized and its properties compared with its precursors as pyrene and 1-bromopyrene. Spectral measurements were performed in solution (methanol, chloroform, cyclohexane) and in polymer matrices as polystyrene, polymethyl methacrylate and polyvinylchloride. Absorption spectra of the probe exhibited less resolved vibrational spectra as its constituents as pyrene or 1-bromopyrene. Absorption spectra of the probe have got similar shape in solvents as well as in all used polymer. Fluorescence spectrum of the probe represents a broad band without any vibrational structure in all solvents and polymers matrices. The vibrational structure of fluorescence of pyrene and 1-bromopyrene under the same conditions is well preserved in absorption as well as in emission spectra. Quantum yield of fluorescence of the probe is slightly higher than anthracene in methanol. The quantum yield of the probe relative to anthracene lies in the range 2–9 in solvents and polymer matrices and it is influenced by oxygen. The lifetime of fluorescence of novel probe is around 5 ns. The position of the maximum of fluorescence spectra is shifted bathochromically with the concentration of the probe in polymer film, which is not observed for pyrene and 1-bromopyrene under the same conditions. The character of the excited state of the probe is discussed.

1. Introduction

Pyrene itself or its derivatives has gained the reputation as a versatile fluorescence probes for monitoring of photophysical and photochemical processes in various complex systems as micelles [1,2], polymers [3,4] and biological structural units as vesicles, cells [5].

All parameters, which are sensitive to the change of the environment, might be used for this purpose. Application of fluorescence has several advantages due to its inherent high sensitivity and more pronounced medium effect on some parameters of pyrene or its derivatives. This includes ratio of some vibrational bands, ratio of excimer to monomer intensity, quantum yield, lifetime of fluorescence, etc.

Some derivatives, where the pyrene is linked with some other functional unit, might offer additional features. Attachment of the reaction center of sterically hindered amine type to pyrene brings about variation of the intensity due to intramolecular quenching after oxidation of amine to *N*-oxyl [6,7]. Transformation of the sterically hindered amine to hy-drochloride results in increased solubility in polar solvents and this probe was used for characterization of premicellar aggregates of surfactants and polyelectrolytes [8].

A well-known class of compounds is acceptor-substituted derivatives of dimethylaniline, which emit dual fluorescence and relax from a roughly planar conformation (locally excited state (LE) with partial charge transfer character) to a roughly perpendicular one (twisted intramolecular charge transfer (TICT) state with full CT character) [9]. Introduction of bulky electron donating group as 7,15-diazadispiro[5,1,5,3]hexadecane strongly influences the electronic relaxation processes for pyrene chromophore and might open the relaxation route which involves rotation of the bulky substituent in limiting case formation of TICT state. Recently, the intramolecular CT properties of molecules with large donor group as 4-(1-pyrenyl)-benzonitrile has been investigated [10]. Both experimental results and quantum chemical calculations indicate that this pyrene derivative after excitation relaxes by mutual twisting of the two sub-units towards a more planar geometry [10].

In this paper the preparation and spectral properties of this derivatives of pyrene with bulky functional group

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7,15-diazadispiro[5,1,5,3] is described. We expect that the spectral properties (namely position and intensity of fluorescence) of this novel probe will be sensitive to the environment. Therefore, the spectral properties are evaluated in the various environments with the aim to obtain more data for its potential application as the fluorescence probe.

2. Experimental

The structures of fluorescent probe and related derivatives of pyrene are shown in Scheme 1. The details of the synthesis are given below.

2.1. 15-(1-Pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane (Py-PA)

Palladium catalyst $Pd_2(dba)_3$ 0.014 g (0.015 mmol) and tri-*tert*-butyl phosphine 0.03 g (0.12 mmol) was added to the suspension consisting of 1-bromo-pyrene 1.18 g (4.2 mmol), 7,15-diaza-dispiro[5.1.5.3]hexadecane 1.43 g (6.4 mmol) and sodium *tert*-butoxide 0.57 g (5.9 mmol) in dry *o*-xylene under nitrogen. The mixture was heated for 12 h at 130 °C, than cooled and washed with water. Organic layer was separated. After solvent evaporation the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and *n*-pentane 2:1 yielding 0.56 g (31%) of yellow crystals with mp: 79–81 °C.

^{1}H NMR (CDCl$_3$) δ_H 1.3–1.45 (m, 2H, N–CH*H*, axial), 1.3–1.7 (m, 20H, spirocyclohexyl), 1.5–1.7 (m, 2H, N–C*H*H, equaroltial), 7.7 (d, 1H, CH(pyrene), $J = 8.3$ Hz), 7.8–8.1 (m, 7H, CH(pyrene)), 8.55 (d, 1H, CH(pyrene), $J = 9.2$ Hz).

2.2. (15-(1-Pyrenyl)-7,15-diazadispiro[5,1,5,3]-hexadecane)ium chloride (Py-PA-HCl)

This compound was prepared by saturation of the solution of the parent amine (Py-PA) in methanol with gaseous hydrochloride. Yellow powder has mp: 176–178 °C.

Anthracene, pyrene (Lachema, Brno, CR) was zonally refined. 1-Bromopyrene (Aldrich, Germany) was analytical reagent. 1-Oxo-2,2,6,6-tetramethylpiperidine (TEMPO) was product of Aldrich (Steinheim, Germany). 1-Oxo-2,2,6,6-tetramethyl-4-hydroxy piperidine was the same as used previously [8]. Solvents: methanol (Slavus, Bratislava, Slovakia), cyclohexane (Merck, Germany) were for UV spectroscopy. Chloroform, benzene, tetrahydrofuran (THF) Lachema, Brno, were analytical grade reagents.

Polymers: polystyrene (PS) (Krasten, Kaučuk Kralupy a.s., CR, SEC (CHCl$_3$), $M_n = 93\,700$ g mol^{-1}, $M_w/M_n = 2.7$, $T_g = 90 - 100$ °C), polymethyl methacrylate (PMMA) (Považské Chemické Závody, Žilina, SR, $M_v = 1.01 \times 10^5$ g mol^{-1}, $T_g = 105$ °C), polyvinyl chloride (PVC) (Neralit 628, Spolana Neratovice, CR, $M_v = 1.11 \times 10^5$ g mol^{-1}, $T_g = 80 - 85$ °C) were used. Polymer films doped with probes were prepared by casting on a glass plate (28 mm × 35 mm) of the 1 ml solution of polymers and probe in chloroform or tetrahydrofurane (5 g/100 ml). The concentration of probe in polymer films was at two concentrations: low 0.002 and high 0.04 mol kg^{-1}.

Absorption spectra were taken on a M-40 UV-Vis spectrometer (C. Zeiss, Jena, Germany), ^{1}H NMR on 300 MHz spectrometer (Bruker, FRG), mass spectra on HP 597 1A (Hewlett Packard, Palo Alto, USA) and FTIR spectra on Impact 400 (Nicolet, USA). Emission spectra were recorded on a Perkin-Elmer models MP-3L and MPF-4 spectrofluorimeter (Perkin-Elmer, Norfolk, CT, USA), which was connected through interface and A/D converter to ISA slot of PC using home made program for data collection. Program Origin 5.0 (Microsoft) was used for data plotting. Emission of solutions was measured at right angle in a 1 cm cell. The quantum yields were determined relative to anthracene in methanol or chloroform. Emission of polymer films was measured in front-face arrangement to the solid sample holder. The quantum yield in polymer films was determined using anthracene as standard and assuming low sensitivity to the medium. The quantum yields in solution and in film were determined according to the relation [11]:

$$\Phi_F = \Phi_F^S \frac{\int_0^\infty I_F(v)\,dv}{\int_0^\infty I_F^S(v)\,dv} \left(\frac{1 - 10^{-A^S}}{1 - 10^{-A}} \right)$$

where Φ_F^S is the quantum yield of standard, integrals $\int_0^\infty I(v)\,dv$ and $\int_0^\infty I_F^S(v)\,dv$ are the areas under curves of the probe and standard, while $I_F(v)$ and $I_F^S(v)$ is the intensity of fluorescence of probe and standard as function of wave-number, respectively, and A and A^S are absorptions of the probe and standard.

R	Probes
H—	Pyrene
Br—	1-Brompyren
	15(1-pyrene)-7,15-diazadispiro [5,1,5,3] hexadecane **[Py-PA]**
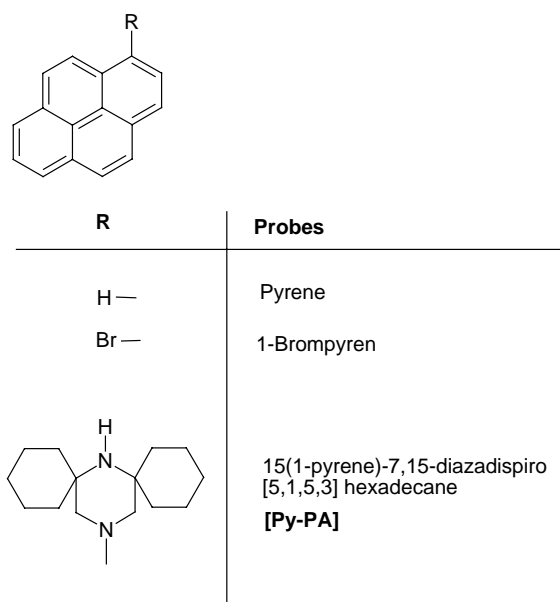
Scheme 1.

Fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, FRG), which operates as a stroboscope. The excitation source was a nitrogen laser ($\lambda = 337$ nm) and emission was selected by the use of cut-off filters. The box-car integrator was connected to PC through interface. The fluorescence decay curves were evaluated by simple phase plane method [12] using program of J. Snyder 1988 based on [13]. The standard deviation, $G^{1/2} = \sum((I_{exp} - I_{calc})^2/n)^{1/2}$, where I_{exp} and I_{calc} are experimental and calculated intensities of emission, respectively, was used to judge the quality of fit. It was assumed that decays were mono-exponential if $G^{1/2}$ is <5%.

Static and time-resolved fluorescence measurements were performed on aerated and de-aerated (10 min purge with argon) solutions. Measurements on polymer films were performed in the presence of air.

3. Results and discussion

The absorption spectra of the probe based on pyrene and directly linked sterically hindered piperazine are shown in Figs. 1 and 2 in different media. Their vibrational resolution is not so well resolved as for parent pyrene or 1-bromopyrene. The loss of vibrational resolution might
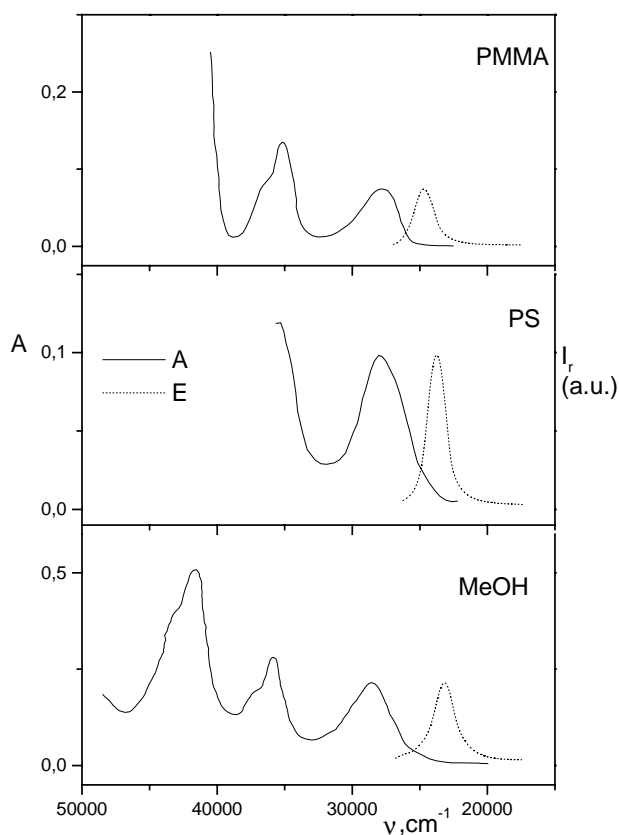

Fig. 1. Absorption (A) and emission (E) spectra of 15-(1-pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane in methanol (MeOH), polystyrene (PS) and poly(methyl methacrylate) (PMMA).
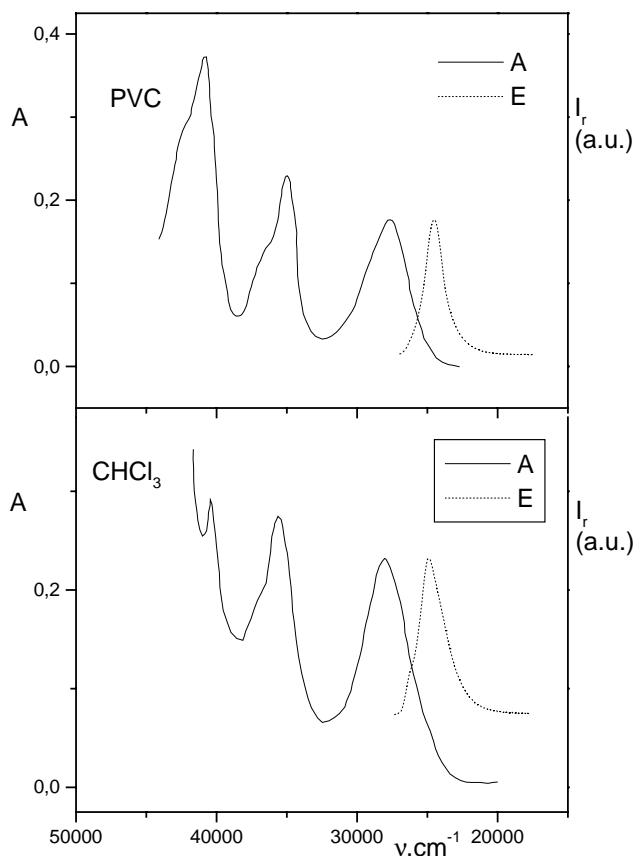

Fig. 2. Absorption (A) and emission (E) spectra of 15-(1-pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane in chloroform and polyvinylchloride.

be due to direct linking of pyrene on piperazine nitrogen, which results in loss of symmetry or electron donating alkyl amino like group on the pyrene frame. The main features of absorption spectra of probe Py-PA are preserved in all environments in solution as well as polymer matrices. There is no distinct shoulder at low wave-number edge of the absorption spectra indicating low energy n–π* state. If such state exists, it is covered by more intense π–π* band at around $28\,500$ cm^{-1}.

The fluorescence of Py-PA probe is one more or less broad band, which has got at high wave-number edge small shoulder in some cases (Figs. 1 and 2). The vibrational structure typical for pyrene and partially preserved for 1-bromopyrene is completely lost for this probe. Some spectral parameters of pyrene, 1-bromopyrene and probe Py-PA are compared in Table 1 for methanol solution and in Table 2 for polymer matrix PMMA. Comparison of some spectral parameters show that the most intense (log $\sim$ 4.5) lowest wave-number band for all three compounds lays around $28\,500$ cm^{-1} and in this region the excitation occurs. The fluorescence spectra exhibit several bands with maximum at $25\,500$ cm^{-1} for pyrene, two bands at $25\,800$ and $24\,800$ cm^{-1} for 1-bromopyrene and one band only for Py-PA below $24\,000$ cm^{-1} position of which is more bathochromically shifted in de-aerated solutions.

Table 1
Spectral characteristics of pyrene and its derivatives in methanol

Probe	ν_{abs}[a] (cm^{-1})	$\log \varepsilon$[b] (mol^{-1} cm^{-1})	ν_{em}[c] (cm^{-1})	Φ_r[d]	τ[e] (ns)	$G^{1/2}$[f] (%)	$\Delta\nu$[g] (cm^{-1})
Pyrene	29000	4.67	26110s[h]	0.40	18.9	4.0	2890
			25510	4.2[i]	389.9[i]	3.9	
1-bromopyrene	28200	4.59	25840	0.08	2.5	2.5	2360
			24880	0.14[i]			
15-(1-Pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane	29040	4.32	23300	7.10	5.7[i]	1.2	5059
			23200[i]	8.55[i]			5838[i]

[a] Maximum of the longest wavelength most intense absorption band.
[b] Decadic extinction coefficient.
[c] Maximum of the emission band.
[d] Quantum yield relative to anthracene in methanol.
[e] Life time of fluorescence.
[f] Standard error.
[g] Stoke's shift.
[h] Shoulder.
[i] De-aerated solution.

The quantum yields relative to anthracene in respective medium are strongly dependent on removing the oxygen by purging the solution with argon for pyrene, less for 1-bromopyrene and Py-PA. Compared to anthracene the values of relative quantum yields are lower for pyrene in aerated methanol but substantially larger for oxygen free methanol (around 4). For 1-bromopyrene the relative quantum yield is 0.1 what is substantially lower for aerated as well as de-aerated methanol. The relative quantum yield of Py-PA indicates that this compound exhibits intense fluorescence from aerated as well as de-aerated methanol. Although pyrene is a structural unit of this probe, oxygen is not able to quench the excited state of this probe as efficiently as excited state of parent pyrene.

The lifetime of pyrene fluorescence strongly depends on de-aeration; it is 18 ns in aerated methanol and 390 ns in de-aerated methanol. Taking into account concentration of oxygen in methanol (2.12×10^{-3} mol dm^{-3} [14]), one can calculate the bimolecular rate constant for quenching $k_q = 2.4 \times 10^{10}$ dm^{-3} mol^{-1} s^{-1}. The lifetime of aerated as well as de-aerated 1-brompyrene is rather short about 2–4 ns. The

lifetime of Py-PA is shorter in aerated (around 4 ns) as compared to deaerated (around 5 ns) solutions.

These features are similar when these three compounds are compared in polymer matrix (PMMA) as it is evident from Table 2. The position of the most intense lowest wave-number band is nearly the same. The vibrational structure of fluorescence of these three compounds is the same in PMMA as in methanol. The relative quantum yields of pyrene and its derivatives in PMMA films are lower than in oxygen free methanol but higher as in aerated one. The lifetime of pyrene in PMMA film in the presence of air is rather long (226 ns). On the other hand, the lifetime of 1-bromopyrene and Py-PA is slightly longer than in solution.

The spectral data for Py-PA in three solvents and three matrices are given in Table 3. This comparison of spectral properties indicates that the basic spectral characteristics of this complex chromophore are preserved in all media under study. The most intense lowest wave-number band in the absorption spectrum is not influenced by the medium. The fluorescence is more intense as compared with anthracene in aerated and de-aerated solutions and polymer

Table 2
Spectral characteristics of pyrene and its derivatives doped in poly(methyl methacrylate) film at concentration 0.002 mol kg^{-1}

Probe	ν_{abs}[a] (cm^{-1})	$\log \varepsilon$[b] (mol^{-1} cm^{-1})	ν_{em}[c] (cm^{-1})	Φ_r[d]	τ[e] (ns)	$G^{1/2}$[f] (%)	$\Delta\nu$[g] (cm^{-1})
Pyrene	29880	3.81	26595	0.84	226.1	2.60	3284
			25773				
			25316				
			24155s[h]				
1-bromopyrene	28920	4.24	25974	0.07	4.4	11.4	2946
			24938				
15-(1-Pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane	28680	3.84	24691	1.20	10.80	5.2	5059

[a] Maximum of the longest wavelength most intense absorption band.
[b] Decadic extinction coefficient.
[c] Maximum of the emission band.
[d] Quantum yield relative to anthracene in poly(methyl methacrylate film) at concentration 0.002 mol kg^{-1}.
[e] Life time of fluorescence.
[f] Standard error.
[g] Stoke's shift.
[h] Shoulder.

Table 3
Spectral characteristics of probe 15-(1-pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane in various media

Medium	v_{abs}[a] (cm^{-1})	$\log \varepsilon$[b] (mol^{-1} cm^{-1})	v_{em}[c] (cm^{-1})	Φ_r[d]	τ[e] (ns)	$G^{1/2}$[f] (%)	Δv[g] (cm^{-1})
MeOH	40880	4.71	23810	7.1	4.7	5.0	5059
	35120	4.45	23200[h]	8.6[h]			5838[h]
	29040	4.32					
CHCl$_3$	39880	4.47	24940	2.2	3.4	7.4	3500
	34920	4.44	24690[h]				3750[h]
	28440	4.36					
Cy	40240	4.83	24100	1.2	3.8	2.3	4060
	33760	4.50	24100[h]	1.9[h]	4.8[h]	1.4	
	28160	4.45					
PS	28320	3.97	23750	9.3	7.6	4.7	4570
			23290[i]				5030[i]
PMMA	35000	4.13	24690	1.2	10.8	5.2	3390
	28680	3.84	23585[i]				5095[i]
PVC	40320	4.57	24500	4.9	9.00	13.6	4060
	34480	4.36	23340[i]				5220[i]
	28560	4.24					

Medium: MeOH (methanol, 10^{-5} mol dm^{-3}), CHCl$_3$ (chloroform, 10^{-5} mol dm^{-3}), PS (polystyrene, 0.002 mol kg^{-1}), PMMA (poly(methyl methacrylate)), 0.002 mol kg^{-1}, PVC (poly(vinyl chloride), 0.002 mol kg^{-1}).
[a] Maximum of the absorption bands.
[b] Molar decadic extinction coefficient.
[c] Maximum of the emission band.
[d] Quantum yield relative to anthracene in the respective medium.
[e] Lifetime of fluorescence.
[f] Standard error.
[g] Stoke's shift.
[h] De-aerated solution (5 min purge with argon).
[i] Concentration of doped probe 0.04 mol kg^{-1}.

matrices. Generally, fluorescence spectrum yields only limited structural information as compared to pyrene because it exhibits a broad band without any vibrational structure. There is however distinct difference in the shape of fluorescence of Py-PA in polar methanol and non-polar cyclohexane (Fig. 3). Clearly the emission band of Py-PA in cyclohexane is narrower and more symmetrical. In methanol the emission band of Py-PA exhibits shoulder and the band is broader. If the emission of Py-PA is quenched in methanol, the maximum is blue shifted (Fig. 4). The quenching of emission of Py-PA in cyclohexane occurs without any shift (Fig. 5). This might be some indication that fluorescence of Py-PA stems
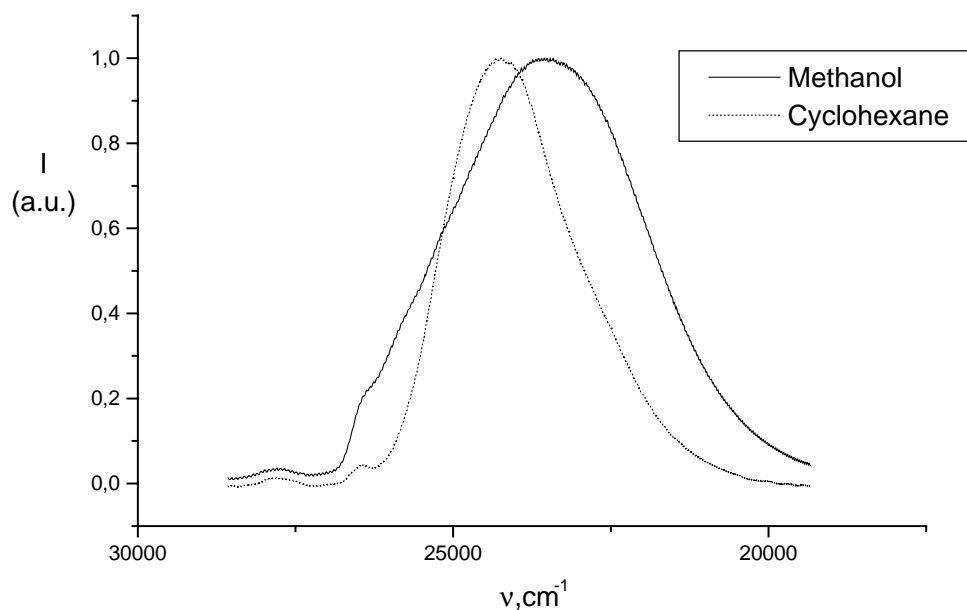

Fig. 3. Emission spectra of 15-(1-pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane in cyclohexane and methanol under argon.
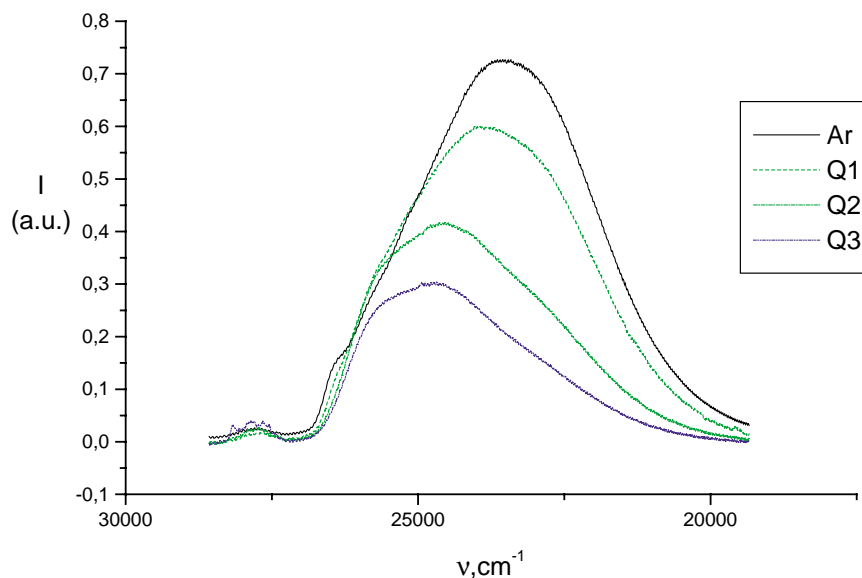
Fig. 4. Emission spectra of 15-(1-pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane in methanol quenched by TEMPO (Q1 = 0.001, Q2 = 0.005 and Q3 = 0.01 mol dm^{-3}).

from two excited state. On the other hand, the fluorescence in both solvents decays mono-exponentially. Moreover, the Stern–Volmer plots for quenching by TEMPO for both solvents based on integrated intensity are well linear which does not support the involvement of two excited states.

The quenching rate constants for intermolecular quenching by *N*-oxyl (TEMPO) and oxygen are summarized for Py-PA and pyrene in Table 4. The values of bimolecular rate constants are at diffusion-controlled limit. Taking into ac-

count the experimental error there is no difference between quenching of simple unsubstituted pyrene and more complex Py-PA. The efficiency of intramolecular quenching with *N*-oxyl could not be performed because oxidation of parent amine Py-PA does not yield the respective radical.

The lifetime lies in the range 3–11 ns and it is slightly longer in polymer matrices (Table 3). If the most intense lowest wave-number band, which is around 28 500 cm^{-1}, is the band where the fluorescence originate, then the Stoke's
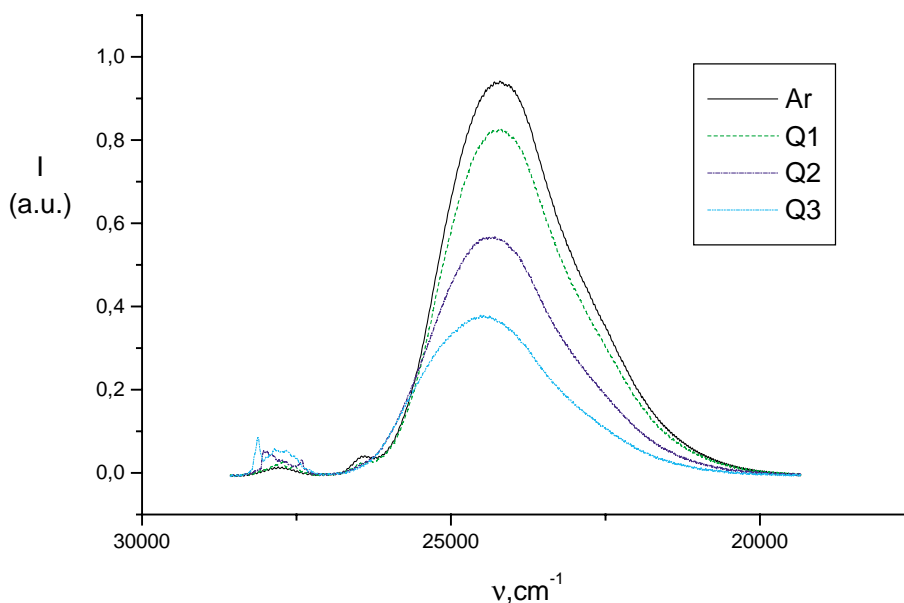

Fig. 5. Emission spectra of 15-(1-pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane in cyclohexane quenched by TEMPO (Q1 = 0.001, Q2 = 0.005 and Q3 = 0.01 mol dm^{-3}).

Table 4
Quenching of pyrene chromophore in different media by oxygen and TEMPO

Substrate	Medium	$K_{SV}(NO)^a$ ($dm^3\,mol^{-1}$)	k_q (NO)[b] ($dm^3\,mol^{-1}\,s^{-1}$)	K_{SV} (O_2)[c] ($dm^3\,mol^{-1}$)	k_q (O_2) ($dm^3\,mol^{-1}\,s^{-1}$)
Py-PA	MeOH	190	3.8×10^{10}	270	5×10^{10}
	Cy	113	2.1×10^{10}	120	2.2×10^{10}
Pyrene	MeOH	3520	0.9×10^{10}	7780	2×10^{10}

[a] Stern–Volmer constant for TEMPO based on plot.
[b] Quenching rate constant calculated using lifetime 5 ns for Py-PA and 390 nm pyrene in methanol.
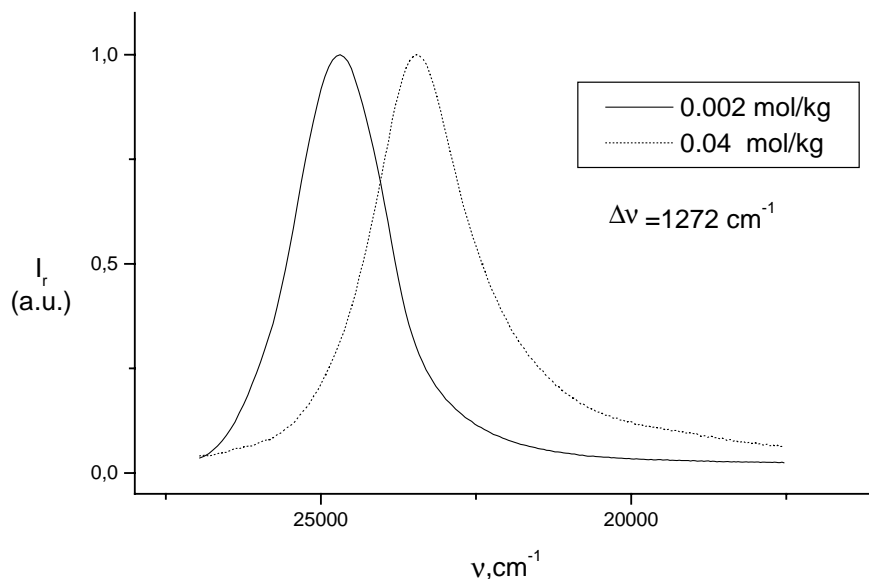[c] Stern–Volme constant based on single point assuming oxygen concentration 0.002 mol dm^{-3}.

Fig. 6. Emission spectra of 15-(1-pyrenyl)-7,15-diazadispiro[5,1,5,3]hexadecane in PMMA at different concentration.

shift is in the range 3000–6000 cm^{-1} indicating that there is large difference in the structure between the ground and the first excited state. At present it is difficult to speculate about the type of change. We can only assume that Py-PA is not planar in the ground state and the planes of both structural units are twisted due to steric reasons. The first excited state can be more planar or more twisted. At present available data do not allow draw any conclusions concerning the type of change. Since the absorption spectra and emission spectra in solvents and polymer matrices are nearly the same one can conclude that relaxation from the first singlet state proceeds both in solution as well as in solid matrix in the same fashion and the microviscosity of polymer matrix does not hinder formation of the relaxed conformation from which fluorescence originates.

The interesting feature of the Py-PA is the concentration dependence of the position of the fluorescence maximum in polymer matrices (Fig. 6). There is bathochromic shift in fluorescence position of Py-PA about 1000 cm^{-1} in concentration range 0.002–0.04 mol kg^{-1} for PMMA and PVC and 500 cm^{-1} for PS. Under the same conditions, pyrene and 1-bromopyrene do not exhibit this effect in these matri-

ces. The simplest explanation is that there is some kind of aggregation in solid polymer matrices. This kind of aggregation should be sub-microscopic scale and it is difficult to prove since the films are optically clear at this concentration of doped probe. It might be assumed that fluorescence of Py-PA is rather sensitive on this type of aggregation. Further studies are needed to prove this property.

In conclusion Py-PA has got some feature that are useful for its consideration as probe. The lowest wave-number absorption band, which accessible for excitation, is not influenced by medium and consequently the same excited state could be reached. In this state the intense fluorescence originates which is not efficiently quenched by air (oxygen), it exhibits reasonable lifetime. There is observed a red shift in fluorescence as a specific response to some kind of aggregation.

Acknowledgements

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