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Spectral properties of bichromophoric pyrene derivatives: Monomer vs. excimer fluorescence

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ABSTRACT

Spectral properties of bichromophoric pyrene probes with different linkage between pyrene units were compared in chloroform, cyclohexane and methanol, as well as in the polymer matrices polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC). The derivatives under study were pyrene, di(1-pyrenylmethyl) ether (DiPyM), 4-(1-pyrenemethoxymethyl) phenylethene (PyS) and 2,3-di(4-(1-pyrenemethoxymethyl)phenyl)butane (DiPyS).

The absorption spectra of the probes exhibited well-resolved bands that were only slightly influenced by substitution and medium. Parent pyrene and PyS, exhibited well-resolved monomer fluorescence in all media, which indicated a weak solvent effect. DiPyM and DiPyS exhibited strong excimer fluorescence in solutions of low viscosity. The influence of the viscosity on the ratio of excimer and monomer emission Φ_{exc}/Φ_{em} of DiPyS and DiPyM in diethylene glycol was also studied. In polymer matrices, only monomer emission of DiPyM and DiPyS was observed. However, the lifetime of monomer emission was influenced by the medium.

1. Introduction

Fluorescence probes based on pyrene as a chromophore have attracted considerable attention over the last decades, and they are widely used for monitoring various processes and functions on a microscopic level [1–5]. Pyrene and its substituted derivatives are the chromophores of choice for this application because of the dependence of their vibrational structure on polarity, the ability to form homo- and hetero-dimers in the excited state (excimers, exciplexes) and their long lifetimes in non-polar media (ca. 400 ns). If these probes have a more complicated structure, aggregation can complicate their application to studies in the solid phase.

The photophysical properties of pyrene excimers have been, in fact, studied over quite a few years [6]. Excimer fluorescence appears if an excited-state molecule associates with a ground-state molecule. The photon is then delocalized over the conjugate to show a net change in fluorescence spectral profile and lifetime [7]. The resultant photophysical properties can be used to derive structural information about the conjugate and, in turn, can lead to an improved understanding of π-stacking interactions. In particular, intramolecular excimer fluorescence is a strong indicator of the spatial proximity of the relevant subunits given that such emission occurs solely from folded rotamers.

A series of dendrimeric compounds bearing pyrene units were synthesized to afford light-harvesting antennae based on the formation of intramolecular excimers [8]. The extent of through-space communication between the pyrene units is modulated by steric interactions imposed by bulky moieties attached at the 6,8-positions of each pyrene unit. This was found for a series of five molecular dyads comprising pyrene-based terminals covalently linked through a 1,3-disubstituted phenylene spacer [9]. Bichromophoric probes, where chromophores like pyrene are linked by a short chain, show dynamic excimer emission, even at high dilution in low viscosity isotropic solutions. In high viscosity solutions or in the solid phase, this excimer emission is completely suppressed. Bichromophoric probes exhibiting excimer emission can provide insight into the micro-viscosity of semi-structured systems.

In the past, we confirmed that di(1-pyrenylmethyl) ether (DiPyM) doped in polymer matrices does not yield any excimer emission [10], but the lifetime was rather sensitive to the polymer matrix. The effect on excimer formation of DiPyM in solvents of low viscosity was employed for monitoring the swelling of interpenetrating polymer networks of polyethylene/poly(styrene-co-butylmethacrylate) in toluene and cyclohexane [11].

In this communication, we report the spectral properties of 2,3-di(4-(1-pyrenemethoxymethyl)phenyl)butane (DiPyS). As for DiPyM, it contains two pyrenes in its molecule, but the arms of the ethane linkage are extended with an oxymethylphenyl unit. Moreover, the ethane linkage was substituted with a methyl group, which may influence free rotation and consequently result in more

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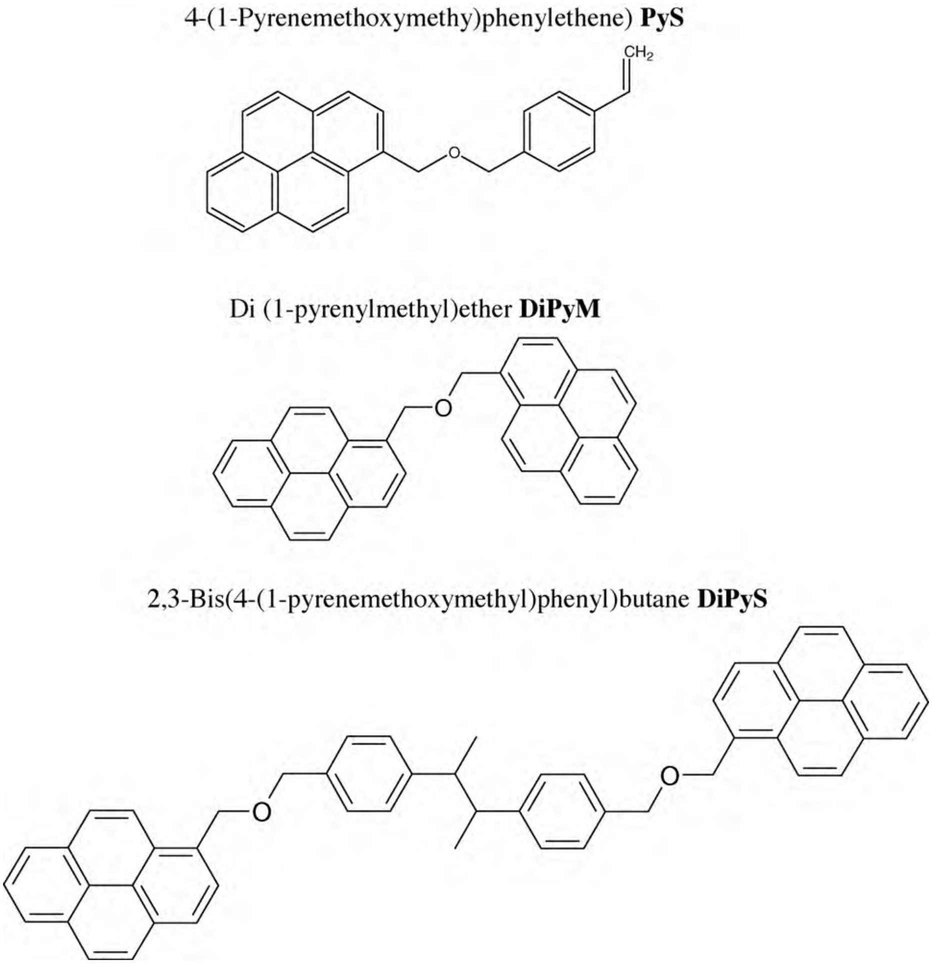


Scheme 1.

difficult excimer formation. Pyrene and a new structural monomer unit, 4-(1-pyrenemethoxymethyl) phenylethene (PyS), were also included in this study (Scheme 1).

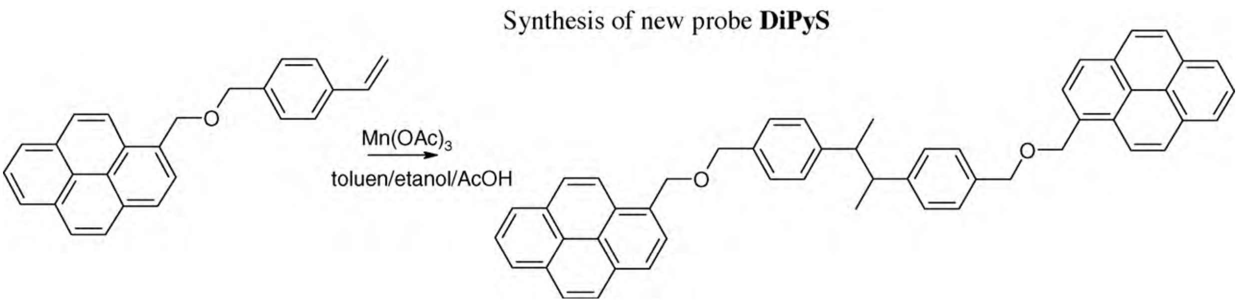
2. Experimental

2.1. Materials

Pyrene and anthracene were zonally refined (Lachema n.e., Brno, CR). Methanol was UV spectroscopy grade. Ethanol, toluene, acetic acid, isohexane, chloroform and tetrahydrofuran were from Slavus (Slovakia), and dichloromethane and chloroform were from Centrachem (Slovakia) and were of analytical grade. All chemicals were used as purchased unless stated otherwise. DiPyM [10] and PyS [11] were the same as described previously. Polymer films doped with pyrene derivatives were prepared by casting from solutions. Films of polystyrene (PS) (Chemische Werke Huels, F.R.G.) and poly(methyl methacrylate) (PMMA) (Diacon, ICI, England) were prepared by casting 1 ml of a chloroform solution of polymer (5 g/100 ml) containing the respective amount of probe on a glass plate (28 mm × 35 mm). The solvent was then slowly evaporated. Films of poly(vinylchloride) (PVC) (Neralit, Spolana Neratovice s.e., CR) were prepared in a similar way by casting from a tetrahydrofuran solution.

2.2. Synthesis

The derivative of pyrene (DiPyS) shown in Scheme 2 was prepared as follows.



Scheme 2.

2,3-Bis(4-(1-pyrenemethoxymethyl)phenyl)butane (DiPyS): 4-(1-Pyrenemethoxymethyl)phenylethene (0.7 g, 2 mmol) and $Mn(OAc)_3$ (0.93 g, 4 mmol) were suspended in 30 mL of the solvent mixture (ethanol/toluene/acetic acid 2:2:1) and stirred vigorously at room temperature. $NaBH_4$ (0.23 g, 6 mmol) was added slowly in very small portions, and the reaction was monitored by TLC. After addition, the mixture was filtered and washed two times with dichloromethane. The organic layers were combined, concentrated and the residue was dissolved in 50 mL of dichloromethane. The solution was washed with aqueous $NaHCO_3$ solution and with water. The organic layer was separated, dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography eluting with 2:1 chloroform/isohexane. Crystallization from methanol afforded DiPyS as yellow crystals (0.57 g, 41%) with mp 182–197 °C. The coupling product was determined to be a 1:1 mixture of diastereomers, as indicated by integration of the methenyl hydrogens at δ 2.80 and 2.95 ppm.

The large interval of the melting point of the product is related to the presence of diastereomers, which can have slightly different physical properties. Despite this fact, purification by column chromatography and consecutive crystallization did not separate the two enantiomers from the racemic mixture.

^{1}H NMR (300 MHz, $CDCl_3$, both diastereomers): $\delta = 1.00$ (d, 3H, CH_3), 1.30 (d, 3H, CH_3), 2.80 (m, 1H, CH), 2.95 (m, 1H, CH), 4.50 (s, 2H, CH_2-phenyl), 4.65 (s, 2H, CH_2-phenyl), 5.10 (s, 2H, CH_2-pyrenyl), 5.30 (s, 2H, CH_2-pyrenyl), 7.05 (d, 2H, phenyl), 7.20 (m, 4H, phenyl), 7.35 (d, 2H, phenyl), 7.90–8.40 (m, 18H, pyrenyl).

^{13}C NMR ($CDCl_3$) δ 146.0, 145.8, 135.9, 135.5, 131.4, 131.1, 130.8, 128.1, 127.8, 127.6, 127.2, 127.0, 125.8, 125.1, 124.4, 123.3, 72.2, 72.0, 70.6, 70.3, 46.9, 46.2, 21.0, 18.3.

FT-IR (KBr, cm^{-1}): 3046, 2961, 2873, 1261, 1092, 1075, 827, 813.

2.3. Spectral measurements

^{1}H NMR and ^{13}C NMR spectra were recorded in solution on a Bruker AC-300P (300.1 MHz) spectrometer, with the TMS proton signal as an internal standard. FT-IR spectra were measured on an Impact 400 (Nicolet, USA). UV–vis absorption spectra were taken on a UV 1650PC spectrometer (Shimadzu, Japan).

Emission spectra were recorded on an RF-5301PC spectrofluorophotometer (Shimadzu, Japan) and a Perkin-Elmer MPF-4 spectrofluorimeter (Perkin-Elmer, Norfolk, CT, USA), which was connected through an interface and A/D convertor to the ISA slot of a PC using a homemade program for data collection. Program Origin 6.1 (Microsoft) was used for data plotting. The fluorescence of solutions was measured in 1 cm cuvettes at a right angle arrangement. The quantum yield was determined relative to anthracene in cyclohexane, chloroform or methanol. The fluorescence of polymer films was taken in a front face arrangement with a solid sample holder. The relative quantum yield of doped polymer films was determined using anthracene as a standard, assuming a small effect of the medium. The relative quantum yields in solution and in films were corrected with different absorptions at the wavelength of excitation [12]. The fluorescence spectra were taken at excitation into the maximum of the longest wavelength absorption band.

The fluorescence lifetime measurements were performed on an LIF 200 (Lasertechnik Ltd., Berlin, F.R.G.), which operated as a stroboscope. The excitation source was a nitrogen laser emitting at 337 nm, and the emission was selected by a cut-off filter. The output signal of the Box Car Integrator was digitized and transferred to a PC using a homemade program. The fluorescence decay curves of pyrene derivatives in aerated solutions were evaluated by the simple phase plane method [13] using the program of J. Snyder based on [14]. The standard deviation $G^{1/2} = \Sigma((I_{exp} - I_{calc})^2/n)^{1/2}$, where I_{exp} and I_{calc} are the intensity of the experimental and calculated emissions, respectively, was used to judge if the decay was mono-exponential. It was assumed that the decay curve satisfied the mono-exponential when $G^{1/2}$ was lower than 5%. Alternatively, the fluorescence decay curves were fitted using an adapted FluoFit MatLab package [15].

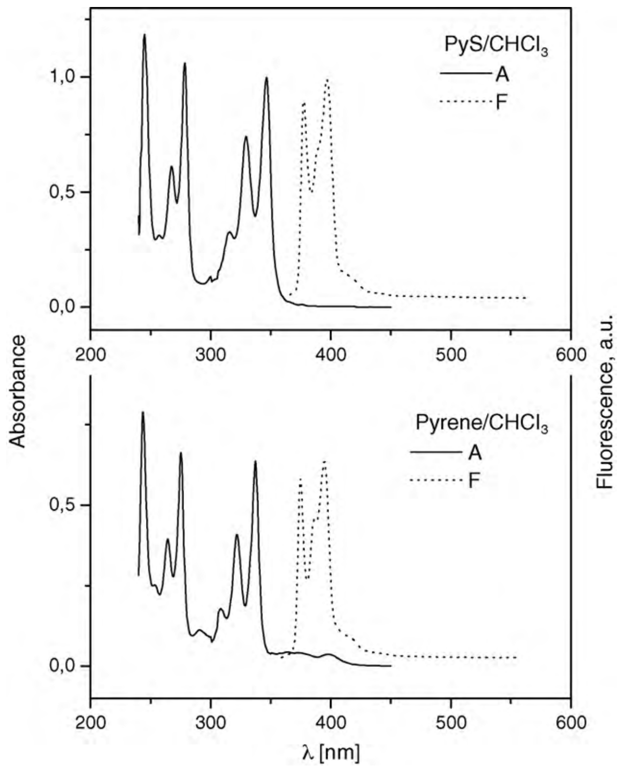


Fig. 1. Absorption and fluorescence of pyrene and PyS in chloroform at 10^{-5} mol dm^{-3}.

The steady state and time-resolved fluorescence measurements were performed in aerated solutions or de-aerated solutions (5 min of bubbling with a stream of nitrogen). All measurements on the polymer films were performed in air.

3. Results and discussion

Comparison of absorption spectra of pyrene and mono-substituted derivatives of pyrene, such as the new monomer 4-(1-pyrenemethoxymethy)phenylethene (PyS), in the region of $S_2 \leftarrow S_0$ and higher transitions revealed well-resolved spectra of similar features in solution (Fig. 1). Substituents on the pyrene ring had negligible effects on the absorption and emission spectra. The absorption spectrum of PyS was slightly red-shifted by 2–4 nm. The same conclusion followed from comparison of the spectra of pyrene and DiPyS (Fig. 2). Moreover, the absorption spectrum of DiPyS revealed no interaction between the pyrenyl chromophores in this spectral region. DiPyM and DiPyS exhibited the same absorption spectrum in solution and in a solid polymer matrix of PMMA (Figs. 3 and 4), and no differences were observed in the PS and PVC matrices either.

The long wavelength $S_1 \leftarrow S_0$ transition, which is observed at around 370 nm as a weak shoulder at a concentration 10^{-5} mol dm^{-3} in solution and 0.002 mol kg^{-1}, was not observed. At a higher concentration (10^{-3} mol dm^{-3}), DiPyM and DiPyS exhibited distinct bands as shoulders at the long wavelength edge at 375 and 395 nm, with $\log \varepsilon \sim 3$.

In general, the changes in absorption spectra of the pyrene derivatives under study were small so that no conclusions concerning any ground-state interaction in the bichromophoric derivatives could be made. The spectral features of the pyrene derivatives in

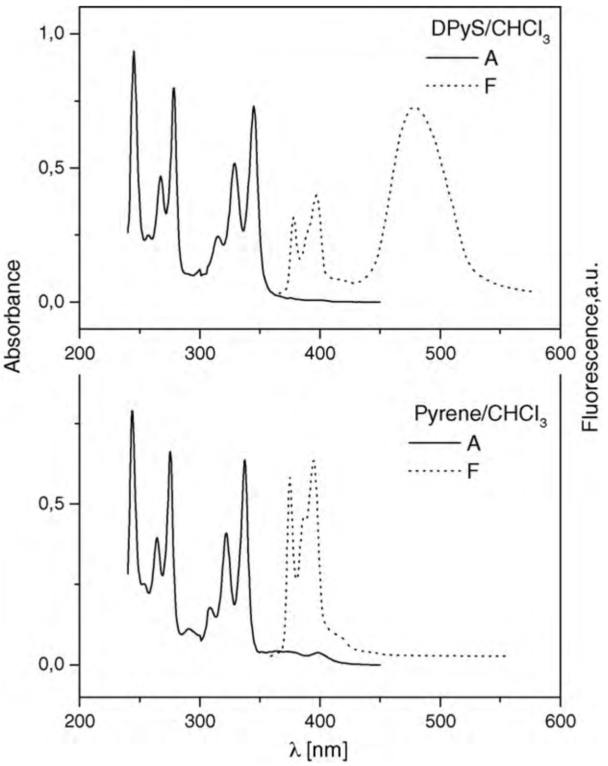


Fig. 2. Absorption and fluorescence spectra of pyrene and DiPyS in chloroform at 10^{-5} mol dm^{-3}.

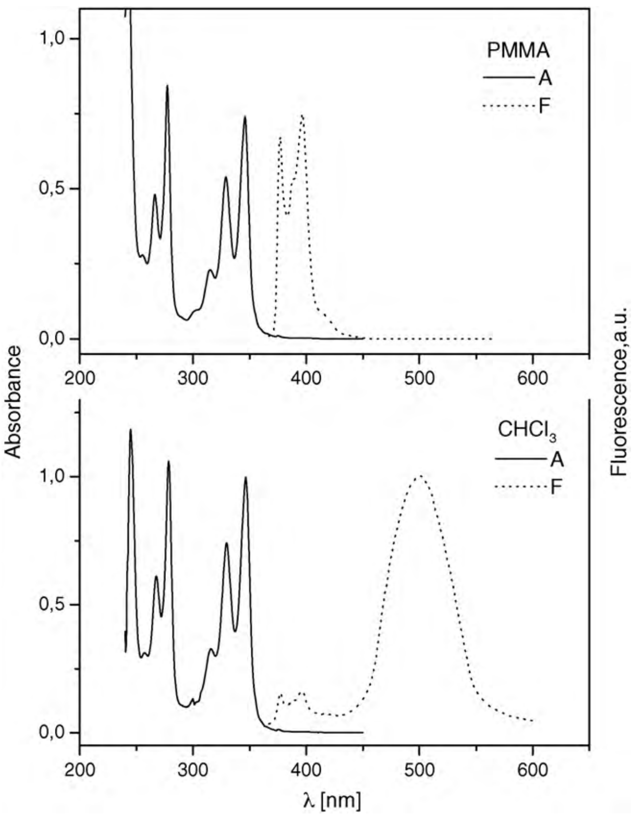


Fig. 3. Absorption and fluorescence of DiPyM in chloroform (10^{-5} mol dm^{-3}) and PMMA (0.002 mol kg^{-1}).

chloroform are summarized in Table 1. In Table 2, the main spectral features of the new bichromophoric compound DiPyS are given.

The fluorescence spectra of pyrene and its derivatives showed vibrationally well-resolved fluorescence in the region of 375–420 nm, which corresponds to monomeric species (Fig. 1). A broad red-shifted excimer fluorescence band was observed for the bichromophoric compounds DiPyM and DiPyS in the region of 450–500 nm (Figs. 2–4). In the monomeric region, vibrational bands appeared at around 377–380, 385–390, 395–400 and 410–415 nm. The relative intensity of these bands depended on the medium. The most intense bands for pyrene are usually at 386 and 396 nm in non-polar media, and the band at 377 nm is less intense. On the other hand, the band at 377 nm is the more intense one in polar media like methanol and PVC (Table 2). The solvent polarity depen-

Table 1
Spectral characteristic of substituted derivatives of pyrene in chloroform solution at concentration 10^{-5} mol dm^{-3}.

Fluorophore	λ_A[a] (nm)	λ_F[b] (nm)	Φ[c]	Φ(Ar)[d]	τ[e] (ns)	τ(Ar)[f] (ns)
Pyrene	337	374, 385, 394, 415	0.04	0.52	11.7	150.1
DiPyM	346	376, 390, 397, 502	0.10	0.81	13.6	56.5
PyS	345	377, 389, 396, 414	0.07	0.45	11.2	122.8
DiPyS	345	378, 389, 397, 479	0.12	1.00	18.1	75.5

[a] Wavelength of maximum absorption.
[b] Wavelength of maximum fluorescence excited at the maximum of absorption.
[c] Quantum yield in aerated solution calculated from Φ of anthracene; $\Phi_{\text{Anthracene}} = 0.2$.
[d] Quantum yield in de-aerated solution.
[e] Lifetime of fluorescence.
[f] Lifetime of fluorescence in de-aerated solution.

Table 2
Spectral characteristics of DiPyS in different media at concentration 10^{-5} mol dm^{-3}.

Medium	λ_A[a] (nm)	λ_F[b] (nm)	Φ[c]	Φ(Ar)[d]	$\Phi_{\text{exc}}/\Phi_{\text{em}}$[e]	$\Phi_{\text{exc}}/\Phi_{\text{em}}$(Ar)[f]
Cyclohexane	343	375, 386, 406, 474	0.11	0.35	8.13	11.81
MeOH	342	374, 380, 385, 407 475	0.16	1.00	6.12	6.01
$CHCl_3$	345	375, 380, 386, 394, 416 477	0.12	1.00	7.81	11.02
CH_3CN	342	375, 380, 386, 394, 414 477			9.41	11.66

[a] Wavelength of maximum absorption.
[b] Wavelength of maximum fluorescence excited at the maximum of absorption.
[c] Quantum yield in aerated solution calculated from Φ of anthracene; $\Phi_{\text{Anthracene}} = 0.2$.
[d] Quantum yield in de-aerated solution.
[e] The ratio of excimer emission Φ_{exc} and monomer emission Φ_{em}.
[f] The ratio of excimer emission Φ_{exc} and monomer emission Φ_{em} in de-aerated solution.

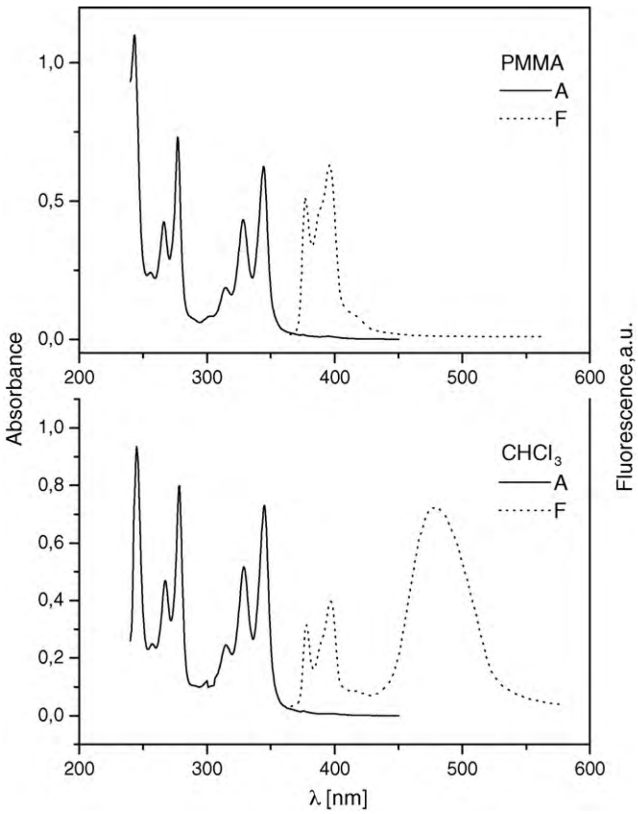


Fig. 4. Absorption and fluorescence spectra of DiPyS in chloroform (10^{-5} mol dm^{-3}) and PMMA (0.002 mol kg^{-1}).

dence of DiPyS indicates a clear correlation between the empirical *py* scale [16]. The relative band intensities of DiPyS emission are strongly dependent on the polarity of the local medium. The I/III band ratio where the I band is $S_1{}^{\nu=0} \rightarrow S_0{}^{\nu=0}$ transition and the III band is $S_1{}^{\nu=0} \rightarrow S_0{}^{\nu=1}$ transition reach the value 0.47 in non-polar cyclohexane and 1.0 in polar methanol.

Bichromophoric probes DiPyM and DiPyS give mostly excimer emission (Figs. 2–4) in solvents like cyclohexane, methanol and chloroform. The maximum excimer fluorescence is shifted from 502 nm for DiPyM in chloroform to 479 nm for DiPyS (957 cm^{-1}). The half-width of the broad excimer band was larger for DiPyM (2620 cm^{-1}) as compared with DiPyS (2320 cm^{-1}), which indicates a more relaxed structure of DiPyM. One would expect the more relaxed structure of the excimer forming state for DiPyS because of the longer arms and closer linkage of the two arms, which is an ethane tether. It is likely that the conformation of DiPyS that leads to excimer emission is tighter than that of DiPyM.

The ratio of excimer and monomer emission $\Phi_{\mathrm{exc}}/\Phi_{\mathrm{em}}$ of DiPyS was studied in solvents with different polarity (Table 2). Excimer emission was significantly more intense in all environments, and $\Phi_{\mathrm{exc}}/\Phi_{\mathrm{em}}$ reached values from 6.12 in methanol to 9.41 in acetonitrile. Additionally, the ratio $\Phi_{\mathrm{exc}}/\Phi_{\mathrm{em}}$ was rather high in de-aerated solutions. This indicates that the quenching of excimer emission by oxygen is more efficient. Only the presence of oxygen in protic methanol had no effect on the ratio $\Phi_{\mathrm{exc}}/\Phi_{\mathrm{em}}$.

Conversely, monomeric emission was exclusively observed from both probes in glassy polymer matrices below T_g (PS, PMMA, PVC), with no excimer fluorescence. The structure of the vibrational bands of DiPyS (Table 3) in the monomeric region in polymer matrices was very similar to pyrene and PyS in solution and in polymer matrices.

The quantum yields of fluorescence Φ in aerated and de-aerated solutions, as well as polymer matrices, based on anthracene (assuming its quantum yield in all of the media under study is 0.2) were rather low in aerated solutions, at about 0.1 (Table 1), but high in de-aerated solutions as well as in the polymer matrices even in the air. The fluorescence quantum yields of DiPyS were high in polar solvents and in PVC, up to 1.00 in some cases (Tables 2–3). Some attention was paid to the fluorescence in aerated solution because in some applications the presence of air is difficult to exclude. Even under aerated conditions, the fluorescence of DiPyS seemed to be quite intense.

The lifetime of fluorescence was around 150 ns in the case of monomeric fluorescence in de-aerated solution as well as in polymer matrices. In aerated solution, it was in the range of 10–20 ns. The lifetime of fluorescence of DiPyM and DiPyS in solution was shorter, at 50–80 ns (Figs. 5 and 6, Tables 1–3).

To compare the sensitivity of DiPyS and DiPyM based on the viscosity of the environment, the temperature-dependent fluorescence was analyzed in diethylene glycol and glycerol (Fig. 7, Tables 4 and 5). The spectral properties of both probes in glycerol were almost identical to those in a polymer matrix, and only

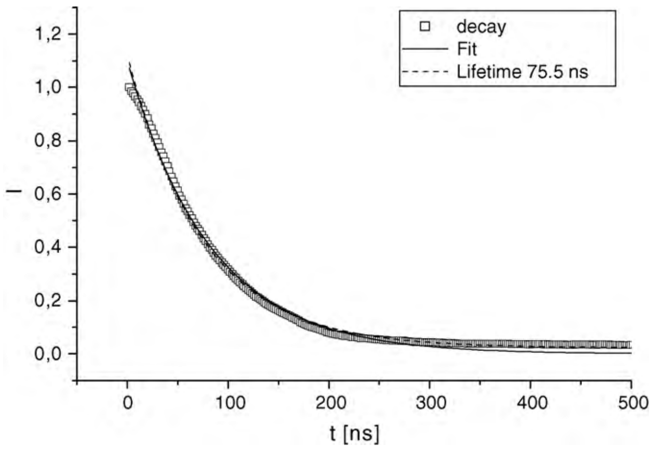


Fig. 5. Fluorescence decay of DiPyS in de-aerated chloroform.

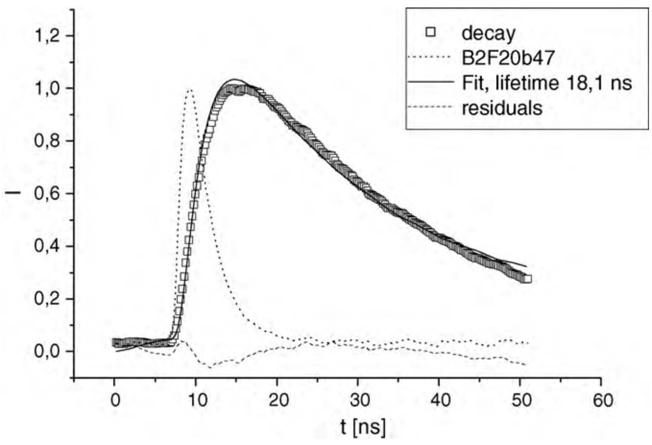


Fig. 6. Decay of fluorescence of DiPyS in aerated chloroform.

Table 3
Spectral characteristics of DiPyS in polymer films at concentration 0.002 mol kg^{-1}.

Medium	λ_{F}[a] (nm)	λ_{Em}[b] (nm)	Φ	τ (ns)
PS	347	379, 391, 398, 419	0.28	151.9
PMMA	345	378, 391, 397, 479	0.50	141.1
PVC	347	378, 390, 397, 415	1.00	93.9

[a] Wavelength of maximum absorption.

[b] Wavelength of maximum fluorescence excited at the maximum of absorption.

Table 4
Spectral characteristics of DiPyS in diethylene glycol at concentration 10^{-5} mol dm^{-3}.

Flurophore	Medium	Temperature (°C)	λ_A[a] (nm)	λ_F[b] (nm)	Φ_{exc}/Φ_{em}[c]	Φ_{exc}/Φ_{em}(Ar)[d]
DiPyS	Diethylene glycol	5	343	375, 381, 386, 395, 415, 474	0.21	0.22
		10	343	375, 381, 386, 396, 415, 474	0.26	0.26
		20	343	375, 381, 386, 396, 416, 474	0.36	0.38
		30	343	375, 381, 386, 396, 417, 474	0.51	0.53
		50	343	375, 381, 386, 396, 418, 474	0.82	0.82
		70	343	375, 381, 386, 396, 418, 474	1	1.02

[a] Wavelength of maximum absorption.
[b] Wavelength of maximum fluorescence excited at the maximum of absorption.
[c] The ratio of excimer emission Φ_{exc} and monomer emission Φ_{em}.
[d] The ratio of excimer emission Φ_{exc} and monomer emission Φ_{em} in de-aerated solution.

Table 5
Spectral characteristics of DiPyM in diethylene glycol at concentration 10^{-5} mol dm^{-3}.

Flurophore	Medium[a]	Temperature (°C)	λ_A[a] (nm)	λ_F[b] (nm)	Φ_{exc}/Φ_{em}[c]	Φ_{exc}/Φ_{em}(Ar)[d]
DiPyM	Diethylene glycol	5	345	375, 381, 386, 415, 480	0.13	0.13
		10	345	375, 381, 386, 415, 481	0.16	0.17
		20	345	375, 381, 386, 416, 484	0.27	0.29
		30	345	375, 381, 386, 417, 486	0.42	0.41
		50	345	375, 381, 386, 419, 488	0.74	0.72
		70	345	375, 381, 386, 420, 489	0.85	0.85

[a] Wavelength of maximum absorption.
[b] Wavelength of maximum fluorescence excited at the maximum of absorption.
[c] The ratio of excimer emission Φ_{exc} and monomer emission Φ_{em}.
[d] The ratio of excimer emission Φ_{exc} and monomer emission Φ_{em} in de-aerated solution.

monomer emission was observed at room temperature. In diethylene glycol, with increasing temperature and lower viscosity of the solvent, excimer emission grew (Fig. 8). The ratio of excimer and monomer emission Φ_{exc}/Φ_{em} of the DiPyS was higher than DiPyM at all temperatures. The maximum value of this ratio was 1.02 for DiPyS and 0.85 for DiPyM at 70 °C. Additional increases in temperature did not change the fluorescence. The most significant difference in the ability to form DiPyS and DiPyM excimers appeared at lower temperatures, such as 5 °C. DiPyM at this temperature formed only 12% excimer, while excimer formation of DiPyS was almost twice as high (22%).

In conclusion, two new pyrene containing probes were spectrally characterized. PyS, which is a styrene-like monomer, has potential use in macromolecules and the monitoring of microenvironments. DiPyS had similar spectral properties to DiPyM, but due to its longer arms, it exhibited more sensitivity to the microviscosity of the environment. Although the arms of DiPyS are longer and more complex, conformations that can yield excimers are likely more favorable.

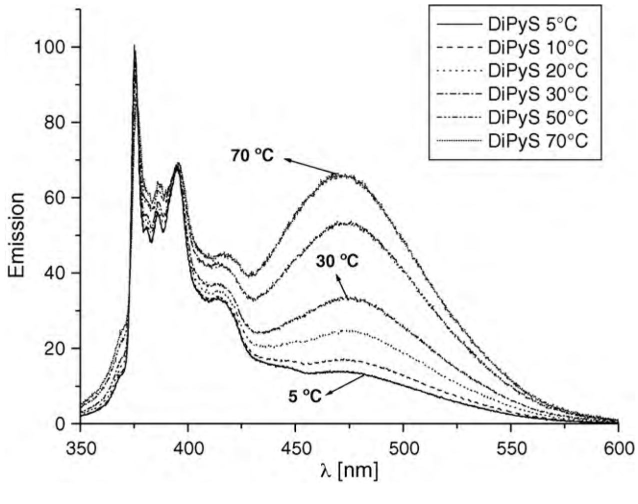


Fig. 7. Temperature-dependent fluorescence of DiPyS in diethylene glycol at concentration 10^{-5} mol dm^{-3}.

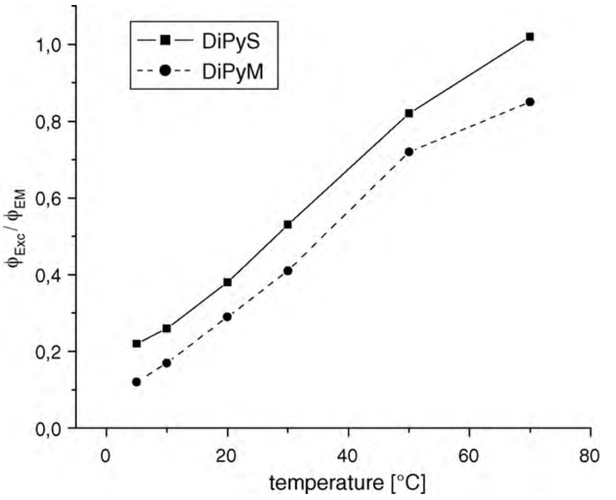


Fig. 8. Dependency plot of the excimer and monomer emission Φ_{exc}/Φ_{em} of DiPyS and DiPyM vs. temperature in diethylene glycol.

Acknowledgments

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