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Pyrene-Doped Polyorganosiloxane Layers over Commercial Glass Fibers

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ABSTRACT

Commercial glass fibers have been subjected to different activation treatments under neutral and acidic conditions to achieve different coating degrees when silanized with γ -aminopropyltriethoxysilane (APES). A fluorescent sulfonamide (PSA) was formed between the amine residue and a fluorescent probe, pyrenesulfonyl chloride (PSC). Reflectance UV-Vis spectra of the pyrene-doped fibers show that pyrene is present in the form of preassociated dimers when the coating degree is low. Emission and excitation fluorescence spectra reveal the existence of a charge transfer ground-state complex with excimer emission at 460-515 nm and absorption red-shifted with respect to the $S_0 \rightarrow S_1$ transition. Lifetime measurements yield three lifetimes, which are assigned to dimer, excimer, and monomer emission. From the photophysical data it is concluded that the fibers with the highest silane content have an open structure with the highest fraction of isolated fluorescent moieties.

KEYWORDS

Pyrenesulfonyl chloride; glass fibers; APES; excimer emission.

INTRODUCTION

Organofunctional silanes are used as coupling agents for improving the bonding between reinforcements and the polymer matrix in composite materials; one of the most widely used, for epoxy-glass systems, is γ -aminopropyltriethoxysilane (APES). In this type of materials it is very important to control the thickness and morphology of the APES layers on the glass surface since these properties are directly related to the in-service behavior of the final composite material [1,2].

A number of papers have been published dealing with the uses of APES and many other silanes in applications such as immobilization of molecules of biological interest, immobilization of inorganic catalysts, modification of electrodes, chromatography supports, and building foundations for self-assembly [3-5]. Many techniques have been used for the characterization of the polyorga-

nosiloxane layers over glass-fiber substrates: Fourier transform infrared spectroscopy (FTIR) [6,7], X-ray photoelectron spectroscopy (XPS) [8-10], and secondary ion mass spectroscopy (SIMS) [11]. But questions about the local molecular arrangement of polysiloxanes or the accessibility of small molecules through the coupling region are not fully understood yet.

Fluorescence of probes and labels can be used as a simple analytical technique to study microdomains due to the known sensibility of their luminiscence to, among other properties, the polarity and rigidity of the local medium [6]. Pyrene and its derivatives are very frequently used probes in fluorescent studies of polymer systems [12,13]. Pyrene has a long singlet lifetime, forms excimers, and acts as an energy acceptor in nonradiative energy transfer from several donors, and its emission vibronic structure is sensitive to the environment. Therefore, pyrene is a very suitable probe for sensing the local polysiloxane molecular arrangement and polarity.

In this work, activated E-glass fibers were silanized with a 1% (v/v) APES aqueous solution and labeled with

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a pyrene derivative (pyrene sulfonylchloride; PSC). The PSA photophysical behavior in this system was studied and this information was used to study the influence of different activation pretreatments of the glass fibers on the structure of the aminosilane coupling region.

EXPERIMENTAL

Glass fiber was supplied by Vetrotex (Spain) and calcinated at 450°C for 1 h to remove organic matter prior to use. All chemicals have been synthesis grade.

Activation

Fibers were subjected to two activation processes: (i) treatment with boiling water and (ii) reflux with 10% HCl aqueous solutions. Activation times and samples codes are summarized in Table I. After acid activation all samples were repeatedly washed with distilled water until Cl⁻ removal, dried at 110°C for 1 h, and kept in a desiccator until silanization.

Silanization

Silanization of activated fibers was performed using a 1% (v/v) γ -aminopropyltriethoxysilane (APES) aqueous solution during 10 min. Polymerization of silanized fibers was performed at 110°C for 1 h in an oven, and afterward they were subjected to Soxhlet extraction with dried toluene for 16 h and vacuum dried for 12 h. Silanized samples were stored in a desiccator until pyrenization.

Labeling Procedure

Well-dried silanized glass fibers were put in contact for 10 min, at room temperature, with 1-pyrenesulfonyl chloride (PSC) solution (10^{-4} M) in acetonitrile (AcN). Then the fibers were subjected to Soxhlet extraction with dried toluene for 16 h and vacuum dried for 12 h.

Table I. Activation and Sample Codes

Sample	Activation reagent	Activation time (h)
F-A	None	None
F-B	Water	1
F-C	HCl, 10%	1
F-D	HCl, 10%	3

Absorption Measurements

Absorption spectra were taken on a Perkin Elmer Lambda 14 equipped with a reflectance spectroscopy accessory. Measurements were performed with the sample at 0° using a Spectralon calibrated diffuse reflectance standard. Because of the very highly absorbing surfaces below 300 nm, spectra were taken on samples with and without PSA and subtraction was made.

Fluorescence Measurements

Steady-state fluorescence measurements were performed on a Perkin Elmer LS-50 fluorimeter. Front-face excitation was employed for solid samples. Spectral conditions were 4-nm excitation and emission slits, a scan speed of 60 nm/min, λ_{exc} = 330, 340, 350, and 360 nm for emission spectra, and λ_{em} = 400, 440, 460, and 470 nm for excitation spectra; all spectra were corrected for excitation. Emission and excitation spectra were obtained by subtraction of the background spectra of a nonpyrenated glass fiber.

Fluorescence decays of PSA fluorophore were obtained by time-resolved fluorimetry using the single-photon counting technique on a modified PRA fluorimeter. An Edinburgh nF900 flashlamp was employed, with N₂ as filling gas. The optimum lamp conditions were 1.2 atm, 40 kHz, and 6.3 kV; the typical fwhm of the lamp pulse was 1.5 ns. Front-face excitation was employed for solid samples; the excitation wavelength was set at 334 nm and the emission wavelength at 378, 430, 470, and 520 nm for all of the samples; 2×10^4 counts were collected, at least, in the maximum.

RESULTS AND DISCUSSION

Absorption Spectra

In Fig. 1a, the absorption spectra in Kubelka–Munk units of pyrene bound to silanized glass fibers are shown. Spectra were normalized to the maximum for comparison.

Along with the S₂ absorption bands, which appear at about 350 nm, being red shifted about 14 nm with respect to the S₂ transitions of pyrene [14], two more absorption bands can be observed also at lower energies, specifically at 378 and 359 nm. This bands may be assigned to the S₀ → S₁ transition by comparison with the corresponding transitions in the pyrene molecule [14], but in this case they are enhanced because of the disruption of the D_{2h} symmetry characteristic of the pyrene mole-

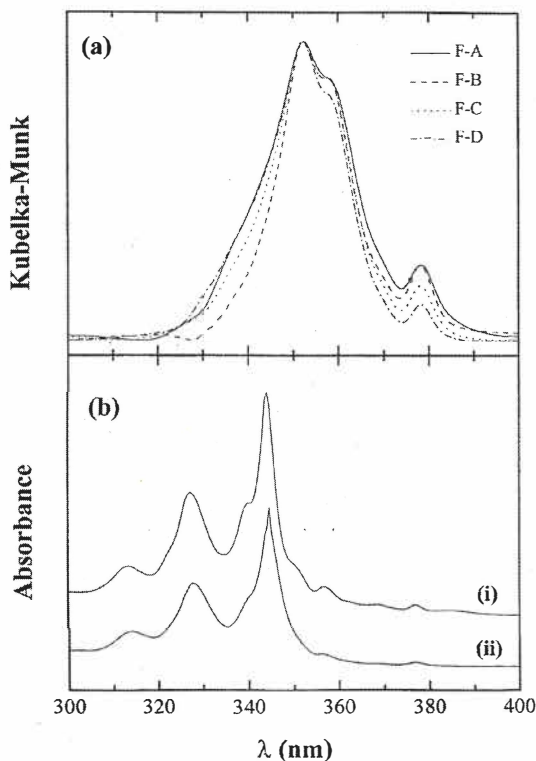


Fig. 1. (a) Reflectance spectra of pyrene attached to silanized glass fibers. (b) Absorbance spectra of cyclohexane PSC solutions (i) with excess and (ii) without propylamine.

cule; the band centered at 378 nm can be assigned to the 0-0 transition.

To verify the above initial assignment, absorption spectra of cyclohexane PSC solutions with an excess and without propylamine are shown in Fig. 1b. The bands at 359 and 378 nm appear to be present in solution but it seems that its absorptivity is much lower than when PSA moiety is attached to the solid. The absorption spectra of PSA become greatly altered when it is chemically attached to a solid substrate such as the glass fibers are. However, the absorption spectra of PSA on the fiber and in acetonitrile solution [12] do resemble one another much more closely than when the former is compared with PSC cyclohexane solutions. It seems that the high polarity of acetonitrile and its very high dipole moment may resemble the polar character of the solid surface and its effects on the absorption spectrum of PSC conjugate; this point needs to be clarified further.

Band Broadening

The broadening of the absorption bands, compared with model systems where pyrene is molecularly dis-

solved, is normally a clear indication of the multiple interactions between the chromophore and the medium, including pyrene association. A convenient relative measure of this loss in resolution can be extracted from the ratio P_A of the absorption intensity of the most intense band to that of the adjacent minimum [13]. The P_A ratio increases in the following order: F-D < F-C < F-B \leq F-A. This result suggests that there is less pyrene association when the activation pretreatment is carried out under acidic conditions and long reaction times. Samples F-A and F-B seem to have the highest fraction of associated pyrene, therefore, samples F-A and F-B have the highest local concentration of amine groups in the surface after silanization.

In previous work [15], using SEM, FTIR, and dynamic contact angle measurements, it was concluded that as a consequence of the different activation treatments, the silane coating degree (amount of silane grafted to the surface per weight of fiber) increases in the following order: F-B < F-A < F-C < F-D. These two observations can be summarized in a single sentence: the higher the coating degree, the less pyrene association. A higher coating degree should lead to a higher surface amine concentration but absorption measurements show an apparently opposite behavior. This discrepancy can be explained in a simple way if it is supposed that for samples F-C and F-D the structure of the polyorganosiloxane layer is an open one; samples F-A and F-B, with a lower total amine content should have a closed structure with a higher local amine content. This conclusion is in good agreement with the three-dimensional poly(aminosilane) network model proposed by Wang and Jones [9] for E-glass slides treated with aqueous solutions of APES.

Emission Spectra

In Fig. 2, the fluorescence spectra at excitation wavelengths 330, 340, 350, and 360 nm are presented for all the samples. Two regions can be observed in each spectrum. The high-energy one, ranging between 360 and 420 nm, corresponds to the PSA monomer emission. The second region consists of structureless broad band, centered at about 470 nm, with two shoulders at about 430 and 520 nm; the former is clearly observed only for the F-B sample. This broad band can be assigned to "excimer-like" emission resulting from contributions of several species which may be present: preformed dimer, exciplex, and excimer emission.

Table II shows some photophysical parameters of interest such as the monomer fluorescence intensity ratio, I_{378}/I_{398} ; the excimer-like fluorescence intensity ratio, I_E/I_M , ($I_M = I_{398}$), and the wavelength corresponding to the

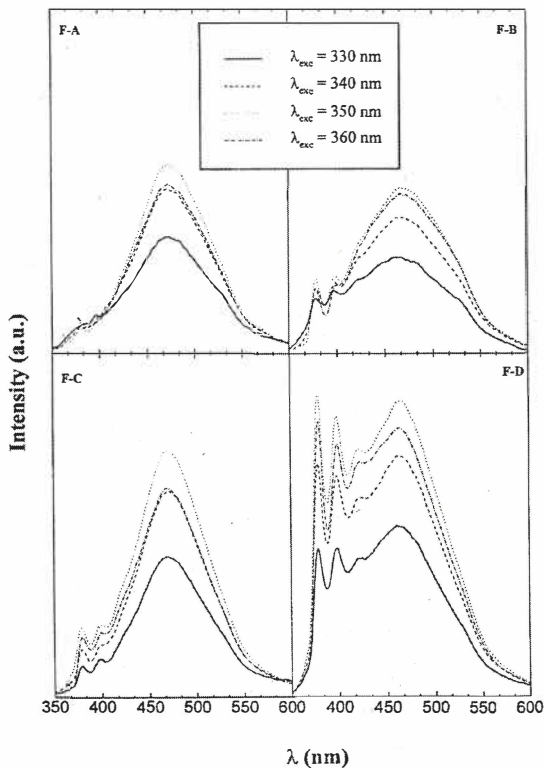


Fig. 2. Fluorescence spectra at excitation wavelengths of 330, 340, 350, and 360 nm of pyrene attached to silanized glass fibers.

Table II. Photophysical Parameters for Different Excitation Wavelengths: the Ratio of the Monomer Band Intensities I_{378}/I_{398} , the Relative Fluorescence Intensity I_E/I_M ($I_M = I_{378}$), and the Wavelength Corresponding to the Maximum Excimer-like Emission λ_E

Sample	λ_{exc} (nm)	I_{378}/I_{398}	I_E/I_M	λ_{em} (max)(nm)
F-A	330	0.64	3.25	471.5
	340	0.70	5.04	471.0
	350	0.70	6.52	472.0
	360	—	—	472.5
F-B	330	0.87	1.57	464.0
	340	0.92	1.98	465.5
	350	0.96	2.19	468.0
	360	0.96	2.43	467.5
F-C	330	0.81	3.91	469.5
	340	0.91	4.08	470.0
	350	0.96	3.50	469.0
	360	0.92	3.31	468.5
F-D	330	1.00	1.15	461.0
	340	1.06	1.09	462.5
	350	1.08	1.06	465.0
	360	1.09	1.06	463.5

maximum excimer-like emission for different excitation wavelengths, λ_E , which can help to discuss the relative importance of the above-mentioned contributions.

It is well known for the pyrene molecule that the fluorescence ratio I_1/I_3 is related to the local polarity [16, 17]. As long as the vibronic structures for both pyrene and PSA are very similar, it can be assumed that the same must be true for PSA. The values of the monomer fluorescence ratio suggest that the local polarity is very similar for all the samples, although sample F-D presents the highest value. This result can be explained if it is taken into account that by FTIR [15] it has been determined that sample F-D has the highest water content and the highest fraction of free silanol groups.

The "excimer-like" fluorescence ratio, I_E/I_M , increases with excitation wavelength for samples F-A and F-B, whereas it remains almost constant for samples F-C and F-D. This result suggests that for samples F-A and F-B, the emitting species at 470 nm may be excited dimers or excited charge transfer complexes, which both absorb at longer wavelengths than the monomer does. On the contrary, for samples F-C and F-D, emission at 470 nm may be associated with excimer or exciplex emission, although other contributions may operate also. In a separate experiment, F-D fibers were immersed in acetonitrile and dimethylsulphoxide and the fluorescence spectra was registered. It was observed that emission at 470 nm is shifted to the red and decreased approximately 10 times. Therefore, for samples F-C and F-D, emission at 470 nm has the characteristics of exciplex emission. This assignment is in accordance with the previous finding; samples activated under acidic conditions give open structures in which the probability of dimer formation and, therefore, excimer emission should be low.

The small shoulder at about 520 nm, which is observed for all the samples, is reported to occur for the pyrenesulphonamide moiety when grafted to polymers in water solution and has been assigned to excimer emission [18]. Nevertheless, the surface picture that the above assignments draw is not compatible with excimer emission because (a) its presence should be restricted to samples F-A and F-B, and (b) the solid nature of the surface makes the excimer dynamics difficult to occur even at room temperature.

To investigate the origin of the red shoulder at 520 nm, the fluorescence spectra of a model compound in solution were recorded. As model compound a low-concentration PSC cyclohexane solution ($7 \cdot 10^{-5} M$) with an excess of propylamine ($\sim 5 M$) was used. In Fig. 3, its fluorescence spectra recorded at different excitation wavelengths are presented. Along with the usual monomer bands, that appear blue shifted about 3 nm with

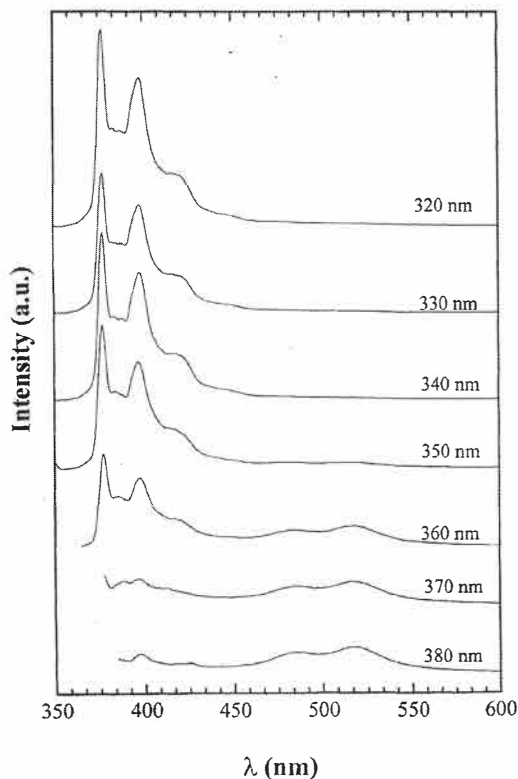


Fig. 3. Fluorescence spectra of a low-concentration PSC cyclohexane solution with an excess of propylamine at different excitation wavelengths.

respect to the monomer emission of glass fibers, there are two new broad bands centered at 480 and 515 nm that become evident when excitation takes place at 360 nm or higher wavelengths. Due to the nonpolar character of the solvent, the low concentration used, and the fact that emission at 515 nm is absent when exciting at the monomer absorption (320–350 nm), we must conclude that these red emissions cannot be associated with either excimer or exciplex emission. As shown below this red emission should be assigned to a charge transfer complex formed in the ground state between the pyrene moiety and the propylamine.

Excitation Spectra

Excitation spectra of samples F–A to F–D at four emission wavelengths are presented in Fig. 4. The general features of these spectra, except for sample F–B, are in accordance with absorption spectra presented in Fig. 1. The maximum intensities are obtained when the emission wavelength is set at 460 nm or higher, except for sample

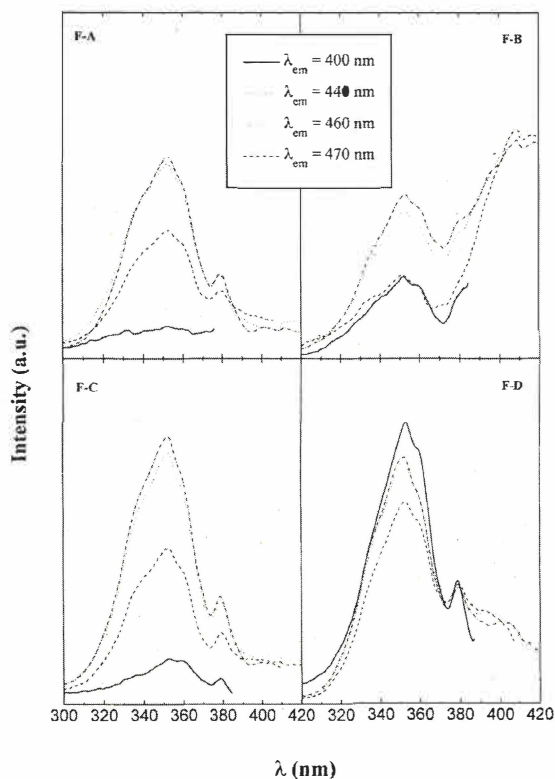


Fig. 4. Excitation spectra of samples F–A to F–D at four emission wavelengths.

F–D, meaning that monomer emission is almost quenched for all samples except sample F–D. In sample F–D, PSA moieties are isolated and this result is in accordance with the surface structure proposed for this sample.

Sample F–B shows a strong band at 390 nm, undetected in the absorption spectra presented in Fig. 1, suggesting that in the region 360–390 nm, absorption of a charge transfer complex takes place. Excitation spectra of the model compound solution, shown in Fig. 5, reveal that at an emission wavelength of 520 nm, a new broad and structured absorption band appears in the region 360–400 nm. This band can be assigned to absorption of a ground-state donor–acceptor charge transfer complex between propylamine and PSA.

Lifetime Measurements

Lifetime decays were performed at three emission wavelengths (378, 430, and 520 nm), setting the excitation wavelength at 334 nm. Although the best fits were obtained when using four-exponential fitting functions, the first time constants were of the order of 200 ps. These

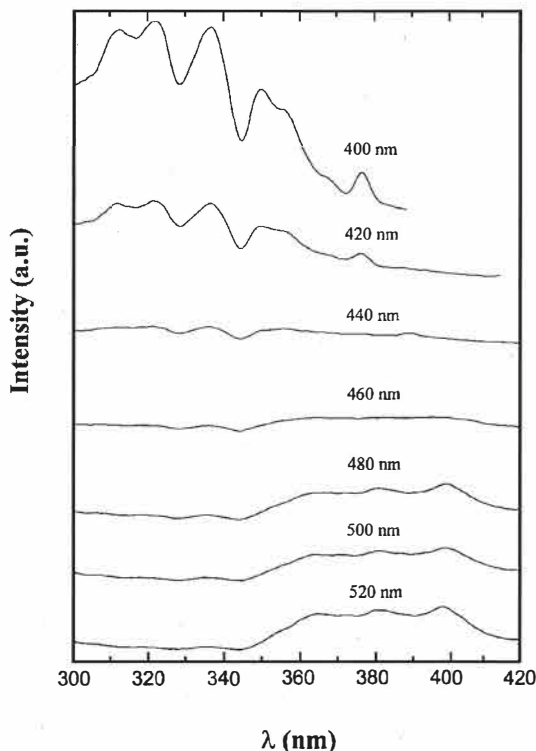


Fig. 5. Excitation spectra of a low-concentration PSC cyclohexane solution with an excess of propylamine at different emission wavelengths.

very short components were assigned to background emission of the glass support, which absorbs below 345 nm approximately. It was eliminated from the fitting and the contributions of the other three components were recalculated; the results are summarized in Table III.

It can be observed that all the lifetimes can be grouped into three components: short (1.0–2.9 ns), medium (5.3–11.0 ns), and long (24.3–36.8 ns). Analysis of the relative contributions as a function of emission wavelength shows that for 378 nm, the largest contribution corresponds to the longest lifetime. w_3 , around 30 ns. The lifetime of pyrenesulfonamides in fluid solutions is reported to be around 30 ns for nonpolar solvents [18], therefore this component may be associated with monomer emission of pyrenesulfonamide moieties.

It can also be observed in Table III that the contribution of the second component is the highest at 520 nm and the shortest one has its maximum contribution at around 430 nm. The second component, around 8 ns, can be tentatively associated with exciplex emission of a charge transfer ground-state complex. The shortest component, around 1.5 ns, can be associated with ground-state

preformed dimers in which the distance or the orientation between the pyrene moieties may be far from the normal parallel arrangement [13].

Because of the solid nature of the samples and because of their pronounced microheterogeneity, fluorescence should come from a distribution of emitting species instead of discrete species; therefore, the three-exponential fit does not give a complete isolation of species, and unfortunately, it is not possible to compare the different contributions as a function of the sample type. Nevertheless, average lifetime values (defined as $\langle \tau \rangle = \sum \tau_i^2 B_i / \sum \tau_i B_i$, where B_i is the statistical weight of component i), obtained at the maximum wavelength of the excimer-like emission (470 nm), can be obtained and compared for the different samples. It can be seen that $\langle \tau \rangle$ increases in the order F–A (16.9 ns) < F–B (18.1 ns) < F–C (20.1 ns) < F–D (29.4 ns). It can be concluded again that the contribution of the shortest species (preformed dimers) to the excimer-like emission is higher for samples F–A and F–B. This result is in accordance with those obtained from absorption and steady-state measurements.

CONCLUSIONS

Model fibers have been prepared with different coating structures by modification of the surface structure and reactivity (number of surface silanol groups) prior silanization. When a reactive fluorescent probe such as pyrenesulfonylchloride is attached to the surface of amine sized glass fibers, its absorption and fluorescent response reveal some important structural details of the coating layer.

Absorption and steady-state fluorescence spectra as well as time-resolved fluorescence results allow us to conclude that the pyrenesulfonyl moiety attached to the amine-coated glass surfaces presents an excimer-like band that arises mainly from dimer and exciplex emission; dimer formation occurs mainly for samples which have not been subjected to acidic pretreatment (F–A and F–B).

When glass fibers are subjected to an acidic activation treatment, the silanization yields the highest coating degree [15], but the local amine concentration seems to be lower than that of fibers with a lower coating extent. This result can be explained if an open surface structure is assumed for acid-pretreated fibers.

Finally, when glass fibers are pretreated under strong acidic conditions (sample F–D), its local micropolarity increases, as measured by the monomer fluorescence ratio.

Table III. Lifetimes, τ_i , Integrated Amplitudes, w_i , and χ^2 Values for Triexponential Fittings of Pyrene Attached to Silanized Glass Fibers at Different Emission Wavelengths

Sample	λ_{em} (nm)	χ^2	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	w_1 (%)	w_2 (%)	w_3 (%)
F-A	378	1.04	—	9.0 ± 0.9	32.6 ± 2.5	—	23.5	76.5
	430	1.20	1.7 ± 0.1	7.6 ± 0.2	32.2 ± 0.7	43.2	34.5	22.3
	470	1.16	2.1 ± 0.1	7.6 ± 0.2	24.8 ± 0.5	35.5	43.1	21.4
	520	1.14	2.2 ± 0.1	7.8 ± 0.2	25.7 ± 0.5	31.2	48.2	20.6
F-B	378	1.39	—	8.1 ± 0.7	29.5 ± 2.4	—	30.9	69.1
	430	1.16	1.0 ± 0.1	5.3 ± 0.5	26.9 ± 1.2	81.5	9.5	9.0
	470	1.09	1.6 ± 0.1	6.5 ± 0.2	27.0 ± 0.8	50.6	33.4	16.0
	520	1.20	2.1 ± 0.1	6.9 ± 0.3	24.3 ± 0.8	41.0	42.9	16.1
F-C	378	1.03	2.4 ± 0.1	8.4 ± 1.0	32.1 ± 3.7	32.6	27.9	39.5
	430	1.04	1.7 ± 0.1	7.2 ± 0.2	33.0 ± 0.7	46.1	33.6	20.3
	470	1.13	2.2 ± 0.1	8.0 ± 0.2	29.6 ± 0.6	36.8	43.1	20.1
	520	1.08	2.5 ± 0.1	7.9 ± 0.2	25.9 ± 0.5	29.2	48.1	22.7
F-D	378	1.09	2.1 ± 0.2	9.7 ± 2.4	33.9 ± 7.4	31.8	22.7	45.5
	430	1.11	1.9 ± 0.1	8.0 ± 0.3	34.4 ± 0.7	40.7	32.1	27.2
	470	1.13	2.4 ± 0.1	10.1 ± 0.3	37.4 ± 0.7	32.8	36.4	30.8
	520	1.23	2.9 ± 0.1	11.0 ± 0.4	36.8 ± 0.7	33.3	41.5	25.2

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