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New Fluorescent Compounds for Plastic Scintillator Applications

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Abstract

The fluorescent compound 3-hydroxyflavone (3HF) has been modified in order to study the resulting structure-fluorescence relationship. A series of twelve derivatives, bearing different substituents at various positions on the phenyl ring, has been synthesized. Each derivative has been tested as a dopant for plastic scintillator applications by incorporating it in a polystyrene matrix. The absorption, fluorescence, and scintillation light yield characteristics of these compounds in polystyrene have been determined. In addition, emission time distributions have been measured and decay time constants have been calculated from these data.

1 Introduction

The new generation of high energy particle accelerators, such as the Superconducting Supercollider (SSC), raises a challenge to existing particle detector technology, since detectors with very fast time response and the ability to withstand exposure to large radiation doses will be required [1]. Due to their short fluorescence decay times, plastic scintillation detectors can exhibit sub-nanosecond timing characteristics. In addition, their relatively low cost and their processibility into many forms allow their use in numerous detector geometries. However, the main drawback to their use in future experiments is their susceptibility to radiation damage [2]. The results reported here are part of an ongoing project that focuses on the investigation and development of radiation resistant plastic scintillators.

Plastic scintillation detectors are based on a polymer matrix doped with fluorescent compounds. When exposed to ionizing radiation, these scintillators emit light characteristic of the fluorescence of the dopants [3]. Standard scintillators use polystyrene (PS) or polyvinyltoluene (PVT) as the polymer base and contain two fluorescent compounds commonly referred to as the primary dopant and the secondary dopant, or wavelength shifter. In such systems, the scintillation mechanism is regarded as a three step process involving (a) excitation of the polymer molecules by ionizing particles passing through the scintillator; (b) transfer of energy from the excited polymer to the primary dopant through the Förster mechanism [4]; and (c) transfer of energy to the secondary dopant through the emission and reabsorption of a photon.

A plastic scintillator's resistance to damage due to ionizing radiation is dependent upon the stability, under irradiation, of both the polymer matrix and the fluorescent compounds. Recent studies [5, 6] indicate that absorption in the blue-violet region of the light spectrum is significantly affected by radiation-induced damage in the polymer matrix. This polymer damage is reflected by increases in its absorption which, for 10 Mrad doses in polystyrene, can extend out to 500 nm. Since most standard plastic scintillators emit in the blue, the damage to the polymer causes a significant decrease in the light yield of the scintillator [7]. The use of new fluorescent compounds emitting in the green/yellow region of the visible spectrum can greatly reduce such light yield losses, since in this wavelength range radiation induced polymer absorption is minimal [8, 9, 10, 11]. Therefore, compounds such

as 3-hydroxyflavone (3HF), which emits at 530 nm, are being investigated as wavelength shifters [8, 12]. 3HF exhibits a large Stokes shift between its absorption (350nm) and emission (530 nm) spectra. This large spectral shift is due to an electronic redistribution in the excited state after intramolecular proton transfer, which is favored by a basicity increase of the carbonyl group in the excited state (Figure 1) [13]. This characteristic makes 3HF an excellent candidate for a different type of plastic scintillator—an intrinsic proton transfer scintillator— [14, 15]. Such scintillators use a single dopant which acts as both primary dopant and wavelength shifter. In other words, a single dopant couples directly to the excited polymer, (polystyrene in our case) and then emits light in the green/yellow region of the visible spectrum. Currently, the drawback of an intrinsic proton transfer scintillator using 3HF is that it has lower light yield than the standard scintillators. Although the quantum yield of 3HF in polystyrene has not yet been determined, the available data indicate that it is considerably smaller than that of fluorescent compounds commonly used in plastic scintillators [16, 17].

Several 3HF derivatives have been prepared in the search for an intrinsic scintillator with high light yield and, in order to make the material more resistant to radiation, one with a large Stokes shift in fluorescence. The present study is a comparative analysis of these derivatives and a characterization of their fluorescence spectra and relative quantum yields. Figure 2 and Table 1 present the list of the 3HF derivatives prepared for this study and the corresponding substitution patterns.

2 Preparation of Scintillators

2.1 Fluorescent compounds

3-Hydroxyflavone (3HF) was purchased from Kodak, recrystallized as needed from a mixture of methylene chloride and hexane, and kept under vacuum in a dessicator. All 3HF derivatives were synthesized following the procedure outlined by Smith *et al.* [18], which is a modification of the Algar-Flynn-Oyamada method for preparation of flavonols [19]. Equimolar amounts of o-hydroxyacetophenone and the corresponding benzaldehyde derivative were dissolved in 95% ethanol in a flask provided with mechanical stirring. A concentrated aqueous sodium hydroxide solution was then poured into the

flask. The reaction mixture turned into a paste which was first let to stand overnight and was then dissolved in an aqueous sodium hydroxide/ethanol mixture. The reaction mixture was then cooled to approximately 15 °C in an ice bath. Next, a 30% hydrogen peroxide solution was added in a ten fold excess to the reaction flask. The reaction mixture was stirred for about six hours, neutralized with a diluted (1 M, $M \equiv mol/Liter$) sulfuric acid solution, and poured into ice cold water. The formed precipitate was collected by filtration and purified by recrystallization from a methylene chloride and hexane mixture. This reaction was also carried out using potassium hydroxide instead of sodium hydroxide. A potassium hydroxide solution prevented the formation of the initial paste. Nevertheless, the use of a mechanical stirrer is recommended since a large precipitate will still form after the hydrogen peroxide addition. The color of each derivative ranged from white to yellow depending upon the nature and the position of the substituent in the phenyl ring. The purity of each derivative was verified using spectroscopic techniques (nuclear magnetic resonance: 1H NMR and ^{13}C NMR) and melting point determinations. Elemental analyses (C, H) were performed for 2C3HF, 4MS3HF, and 4PO3HF, since they had not been previously reported in the literature.

2.2 Sample preparation

Styrene was first deinhibited using a chromatography column (supplied by Aldrich Chemical Co.) to remove *tert*-butylcatechol and was subsequently purified by vacuum distillation. Glass polymerization tubes were cleaned with nitric and sulfuric acids, rinsed with distilled water, and then treated for about 4 hours with a 30% solution of dichlorodimethylsilane in chloroform. Finally, they were rinsed in turn with chloroform, methanol, and distilled water. This treatment builds a hydrophobic Langmuir layer on the walls of the tube which enables the removal of the plastic after polymerization. The appropriate amount of 3HF or a 3HF derivative was then added to the polymerization tubes which were then filled with purified styrene. The various solutions were degassed with repeated freeze-pump-thaw cycles. They were then polymerized in a silicone oil bath using the following temperature profile, 90 °C for 2 hours, 110 °C for 24 hours, 125 °C for 48 hours, 140 °C for 12 hours. The bath temperature was then ramped down to 90 °C at a rate of 10 °C/hour. When the temperature was raised to 125 °C, the solutions

were backfilled with nitrogen to prevent them from boiling. At the end of the polymerization cycle, the test tubes were quenched in liquid nitrogen to facilitate the release of the polymer and avoid the formation of vacuum bubbles. The rods were then cut into discs of 2.2 cm diameter and 1 cm thick and then polished.

For each compound, the optimal doping concentration in polystyrene for intrinsic scintillator application was determined. Scintillator samples of 3HF at doping concentrations from 0.05% to 2% by weight were first prepared. The scintillation light yield for these samples (1MeV electrons were used for excitation) was measured and the yield as a function of concentration tabulated. (Section 3.2 contains more details on this measurement.) The light yield for this set saturated at a concentration of approximately 0.75% by weight, Figure 3. For the derivatives, the optimal concentration was determined based on the optimal doping concentration for 3HF (0.75%) and on the molar absorptivity coefficients of the derivatives relative to that of 3HF. In order to determine the molar absorptivity coefficients, dilute solutions (10^{-4} M) of 3HF and each derivative were prepared following the procedures described above. Absorbance measurements were then performed on these samples. Absorbance is defined as $A = -\log(\frac{I}{I_0})$ and it is assumed that I and I_0 obey the combined Beer-Lambert law:

$$\frac{I}{I_0} = 10^{-\epsilon cl}$$

where I_0 represents the monochromatic light energy incident on a sample containing a single absorbing species of concentration c (moles/liter); I is the light energy transmitted through the sample of length l in cm; and ϵ (liters/mole-cm) is the molar absorptivity coefficient for the species at a given wavelength. Table 2 depicts the photophysical characteristics of 3HF and its derivatives determined using these low concentration samples (see Section 3). For each derivative, the optimal doping concentration was then chosen such that the product of concentration times molar absorptivity coefficient, measured at the wavelength of peak emission for polystyrene (320 nm), equalled that of 3HF ($0.75\% \times \epsilon_{3HF}$).

3 Instrumentation and Techniques

3.1 Absorbance and fluorescence spectra

Absorbance and fluorescence spectra were recorded with a Hewlett-Packard model 8451A diode array spectrophotometer. All absorbance measurements used pure (undoped) polystyrene as the reference. The fluorescence spectra were measured using an external Hg lamp whose light was brought into the spectrophotometer by means of a quartz fiber. An excitation wavelength of 254 nm, 313 nm, or 352 nm could be selected with the use of bandpass filters. With the 254 nm excitation light, back-surface (BS) excitation measurements were performed. In this geometry, light from the quartz fiber excited the sample surface that faced away from the spectrophotometer collection optics. The sample fluorescence is thus viewed through the sample. A 45° angle of incidence with respect to the surface plane was used. These measurements were performed to monitor the overall scintillation process since, at this wavelength, the polymer molecules are first excited and then energy is transferred to the dopant which, in turn, will fluoresce. For each sample, the fluorescence integrated over all wavelengths was measured and compared to that of the parent compound, 3HF. The results from these measurements are expected to be similar to those obtained using ^{207}Bi as an excitation source, since ionizing radiation also excites the polymer which, in turn, transfers part of its excitation energy to the dopant. With the 313 nm or 352 nm excitation light, both back-surface (BS) and front-surface (FS) excitation measurements were recorded. For the latter measurements, the quartz fiber was positioned so that the UV light excited the sample surface facing the spectrophotometer optics. In this case, the fluorescence was viewed directly, i.e., not through the sample. (The angle of incidence was also 45°.) These measurements were made in order to measure the fluorescence of each dopant relative to that of 3HF, since at these long wavelengths polystyrene does not absorb. There should be no difference among the relative quantum yield results from BS and FS excitation measurements since the derivatives exhibit a large Stokes shift between absorbance and fluorescence spectra. Disagreements in the data from 254 nm excitation measurements (or ^{207}Bi) and 313 nm or 352 nm excitation measurements indicate a poor coupling in the energy transfer process between polystyrene and the 3HF derivative.

3.2 Light yield measurements

The scintillators were excited by 1 MeV conversion electrons from a ^{207}Bi source. The scintillation light yield measurements used a Hamamatsu R669 photomultiplier tube (PMT) as the photo-detector. This PMT has a relatively constant quantum efficiency from 430 nm to 600 nm. The scintillator discs were placed directly on the PMT using immersion oil for optical contact. The pulse height spectra were recorded with a LeCroy qVt multi-channel analyzer. Light yield values obtained from these measurements were corrected for the quantum efficiency variations of the PMT over the fluorescence wavelength range of the scintillator being studied.

3.3 Decay time determinations

Emission time distributions were measured utilizing the same method reported earlier [11]. A ^{22}Na source excited the scintillator sample being studied as well as a BaF_2 trigger crystal. The BaF_2 crystal was coupled to a PMT (Hamamatsu assembly H3177) and provides the START signal for a LeCroy qVt operating in time mode. The STOP signal is generated by a single photon from the test scintillator that is detected by a second PMT (Hamamatsu assembly H4022). The geometry is such that typically only single photons from the scintillator under test trigger the STOP signal. The emission time probability distribution for all but one of these intrinsic scintillators can be described by a one exponential decay (eq. (1))

$$E(t) = \frac{1}{\tau_1} e^{-t/\tau_1} \quad (1)$$

where τ_1 is the decay constant. The emission time probability distribution for the scintillator made with the 2MO3HF derivative was best described by a two exponential decay (eq. (2))

$$E(t) = \frac{\frac{e^{-t/\tau_1}}{\tau_1} + \frac{R}{\tau_2} e^{-t/\tau_2}}{1 + R} \quad (2)$$

where τ_1 and τ_2 are the two decay constants and R is the ratio between the two components. For both distributions, a gaussian time error with a standard deviation σ_t was assumed. In either case, the resulting time distribution is

then:

$$P(t) = \int_0^{\infty} E(t') \frac{1}{\sqrt{2\pi}\sigma_t} e^{-(t-t')/2\sigma_t^2} dt' \quad (3)$$

By fitting the above distribution to the data, the parameter τ_1 (τ_1 , τ_2 , and R for the case of 2MO3HF) was determined.

4 Results and Discussion

The intrinsic scintillator samples prepared for this study were of concentrations similar to that used for a primary dopant in standard plastic scintillators and ranged from 0.6–1% by weight. Therefore, the absorption thresholds seen in Figures 4–8 are higher than the values reported in Table 1. These latter values correspond to absorption data from the very low dopant concentration samples that were used to determine the molar absorptivity coefficients. The spectra indicate that the derivatives substituted in the second position of the phenyl ring (*ortho*-substituted derivatives) — 2C3HF, 2F3HF, 2M3HF, 25M3HF, and 2MO3HF — show a hypsochromic shift (shift to shorter wavelengths) relative to 3HF absorption, except for 2MO3HF whose absorption spectrum is similar to that of 3HF. On the other hand, the rest of the derivatives: 4C3HF, 4F3HF, 4M3HF, 4MO3HF, 4MS3HF, 4P3HF, and 4PO3HF (*para*-substituted, substituted in the fourth position of the phenyl ring, derivatives) shift the absorption to longer wavelengths. The different behaviour among the derivatives can be understood by considering the lack of planarity of the molecules in the *ortho*-substituted derivatives. In these derivatives, the substituent introduces a steric hindrance effect that forces the phenyl ring to move out of the plane containing the rest of the molecule and thus decreases conjugation of the π -electron system. Therefore, electron delocalization is less than in the *para*-substituted derivatives where the coplanarity is not disturbed by the presence of the substituent.

The fluorescence spectra (Figures 4–8) show that 3HF and its derivatives fluorescence within a 20 nm range, with 4P3HF and 4MO3HF the compounds emitting at the longest wavelengths. The Stokes shift has significantly decreased for 4MO3HF and 4MS3HF whose absorption extends to very long wavelengths. On the other hand, 2M3HF and 25M3HF present a slightly larger Stokes shift because of their absorption shift to shorter wavelengths. These fluorescence spectra are also representative of the differences

in quantum yield among the derivatives. The *para*-substituted derivatives have light yields similar to that of 3HF. The *ortho*-substituted derivatives, however, have a light output considerably smaller than that of 3HF. In the 3HF molecule, after excited state proton transfer, the molecule relaxes through both fluorescence and vibrational relaxation (radiationless mechanism), which includes torsion of the phenyl ring as one of the active modes [20]. In the *ortho*-substituted derivatives, the phenyl ring is tilted off the plane and in the excited state will be driven towards planarity. After proton transfer, it will return to its original position, thus favoring phenyl ring torsion as a deactivation mode.

Table 3 gives the quantum yield, as determined from four different measurements, of the derivatives relative to that of 3HF. The results obtained using UV light as the excitation source are in agreement within experimental error, except for the *ortho*-substituted derivatives whose values using the 352 nm excitation wavelength are higher than in the rest of the measurements. Using the 352 nm light, the derivatives are directly excited where their absorption is close to the maximum. The decrease seen in the relative quantum yield for the *ortho*-substituted derivatives when 313 nm excitation light is used indicates that these derivatives are not being completely excited at this wavelength. Because of the structural differences between the *ortho*- and the *para*-substituted derivatives, it is likely that the former have an absorption minimum around 300 nm which is not present in the other derivatives. With the 254 nm excitation wavelength, the measurements are more sensitive to surface differences among the samples, since this light is absorbed within a few microns of the sample surface. This explains the large variation in the error for this measurement among the different samples. This measurement also reflects the coupling between polystyrene and the derivatives, which, likewise, depends upon the concentration of the derivatives. The results listed in Table 3 using 254 nm light reflect an increase of the relative quantum yield for the *ortho*-substituted derivatives when compared with the 313 nm light results. However, these values are still slightly smaller than those determined with the 352 nm light. The results obtained with ^{207}Bi as the excitation source demonstrate the same differences among the derivatives, except for 4MO3HF, 4MS3HF, 4P3HF, and 4PO3HF whose measurements reflect no increase in light yield over the parent compound, 3HF.

Table 3 also displays the decay time constant (τ_1) of the intrinsic scintillators prepared with the 3HF derivatives. The decay times range between

8–10 ns and, except for the case of 2MO3HF, have a single component. These times are not very different from that of 3HF. In other studies using 3HF as a wavelength shifter, a slightly faster decay time had been observed. Figures 9 and 10 are representative of the measured time distributions. The curves corresponding to the fits are overlaid on the data.

5 Conclusions

The structure of 3-hydroxyflavone has been modified through substitution in its phenyl ring. The different derivatives prove that it is possible to change the quantum yield of the parent compound by modifying its structure. Among the 3HF derivatives prepared, the *ortho*-substituted derivatives present an absorption threshold similar to or smaller than that of 3HF, and their quantum yield is lower than that of the unsubstituted compound. The *para*-substituted derivatives have their absorption shifted to longer wavelengths relative to the 3HF absorption. The quantum yields of the *para*-derivatives are similar to or larger than that of 3HF. The difference in the quantum yield between the *ortho*- and the *para*-substituted compounds is due to the lack of planarity of the molecule for the *ortho*-substituted compounds, since the steric hindrance caused by the substituent moves the phenyl ring out of plane. Most 3HF derivatives are as fast as the parent compound. The decay times range between 8–10 ns, and are slightly larger than that found when 3HF is used as a wavelength shifter.

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Table 1. List of 3-hydroxyflavone derivatives studied

R ₂	R ₄	R ₅	Name	Description
H	H	H	3HF	3-hydroxyflavone
Cl	H	H	2C3HF	2'-chloro-3-hydroxyflavone
H	Cl	H	4C3HF	4'-chloro-3-hydroxyflavone
F	H	H	2F3HF	2'-fluoro-3-hydroxyflavone
H	F	H	4F3HF	4'-fluoro-3-hydroxyflavone
Me	H	H	2M3HF	2'-methyl-3-hydroxyflavone
H	Me	H	4M3HF	4'-methyl-3-hydroxyflavone
Me	H	Me	25M3HF	2',5'-dimethyl-3-hydroxyflavone
H	MeS	H	4MS3HF	4'-thiomethyl-3-hydroxyflavone
H	Ph	H	4P3HF	4'-phenyl-3-hydroxyflavone
H	PhO	H	4PO3HF	4'-phenoxy-3-hydroxyflavone
H	MeO	H	4MO3HF	4'-methoxy-3-hydroxyflavone
MeO	H	H	2MO3HF	2'-methoxy-3-hydroxyflavone

Table 2. Photophysical characteristics of 3HF and its derivatives in a polystyrene matrix.

Compound ^a	λ_{max}^b (nm)	10^{-4} M threshold (nm)	ϵ^c (L mol ⁻¹ cm ⁻¹)	λ_{em}^d (nm)
3HF	350	390	14000	530
2C3HF	335	390	6000	532
4C3HF	345	395	23000	536
2F3HF	335	385	10000	532
4F3HF	340	393	11000	532
2M3HF	330	385	11000	530
4M3HF	350	393	16000	534
25M3HF	330	388	15000	532
4MS3HF	360	415	20000	545
4P3HF	360	410	35000	548
4PO3HF	350	400	28000	538
4MO3HF	350	403	28000	536
2MO3HF	335	395	10000	534

^aThe concentration of the derivatives in polystyrene is of the order of 10^{-4} M for these samples. ^bMaximum absorption wavelength. ^cAbsorptivity coefficient at wavelength of maximum absorption. ^dMaximum emission wavelength.

Table 3. Decay times and relative light yields of 3HF and its derivatives in polystyrene.

Scintillator ^a	Decay time τ (ns)	Light yield ^b			
		²⁰⁷ Bi β -source	UV 254 nm	UV 313 nm	UV 352 nm
0.75% 3HF	8.53±0.2	1	1	1	1
1% 2C3HF	8.21±0.1	0.64	0.57 (0.07)	0.47 (0.01)	0.71 (0.03)
0.75% 4C3HF	8.70±0.1	1.04	1.07 (0.08)	1.10 (0.02)	1.05 (0.06)
0.6% 2F3HF	8.74±0.1	0.67	0.57 (0.06)	0.56 (0.01)	0.69 (0.02)
0.75% 4F3HF	9.08±0.1	1.04	1.05 (0.11)	1.05 (0.02)	1.05 (0.04)
0.6% 2M3HF	8.65±0.1	0.66	0.65 (0.08)	0.55 (0.02)	0.74 (0.02)
0.75% 4M3HF	8.46±0.1	1.03	1.11 (0.01)	1.15 (0.01)	1.15 (0.04)
0.6% 25M3HF	9.11±0.2	0.65	0.62 (0.07)	0.55 (0.01)	0.75 (0.02)
0.75% 4MS3HF	7.49±0.1	1.01	1.23 (0.08)	1.08 (0.09)	1.21 (0.02)
0.6% 4P3HF	7.92±0.2	1.01	1.30 (0.16)	1.25 (0.01)	1.27 (0.04)
0.6% 4PO3HF	9.11±0.1	0.99	1.25 (0.06)	1.21 (0.02)	1.25 (0.04)
0.75% 4MO3HF	7.47±0.1	0.97	1.18 (0.13)	1.10 (0.03)	1.18 (0.05)
1% 2MO3HF	3.51±0.3 (τ_1) 13.51±0.5 (τ_2) 1.88±0.2 (R)	0.61	0.61 (0.07)	0.49 (0.02)	0.65 (0.03)

^aConcentration of the derivatives is in percent by weight. ^bLight yield results using different excitation sources are relative to 3HF. Standard deviation given in parentheses.

Figure Captions

Figure 1. Excited-state intramolecular proton transfer for 3HF.

Figure 2. Substitution pattern in 3HF.

Figure 3. Light yield as a function of concentration for 3HF intrinsic scintillator samples.

Figure 4. Absorbance and fluorescence spectra of 0.75% 3HF (solid line), 1% 2C3HF (dotted line), and 0.75% 4C3HF (dashed line) in polystyrene. Concentrations in percent by weight. Excitation wavelength 352 nm, BS.

Figure 5. Absorbance and fluorescence spectra of 0.6% 2F3HF (solid line), 0.75% 4F3HF (dotted line) in polystyrene. Concentrations in percent by weight. Excitation wavelength 352 nm, BS.

Figure 6. Absorbance and fluorescence spectra of 0.6% 2M3HF (solid line), 0.75% 4M3HF (dotted line), and 0.6% 25M3HF (dashed line) in polystyrene. Concentrations in percent by weight. Excitation wavelength 352 nm, BS.

Figure 7. Absorbance and fluorescence spectra of 1% 2MO3HF (solid line), 0.75% 4MO3HF (dotted line), and 0.75% 4MS3HF (dashed line) in polystyrene. Concentrations in percent by weight. Excitation wavelength 352 nm, BS.

Figure 8. Absorbance and fluorescence spectra of 0.6% 4P3HF (solid line), 0.6% 4PO3HF (dotted line) in polystyrene. Concentrations in percent by weight. Excitation wavelength 352 nm, BS.

Figure 9. Decay time distribution of a 0.75% 3HF scintillator compared to the fit.

Figure 10. Decay time distribution of a 0.6% 4PO3HF scintillator compared to the fit.

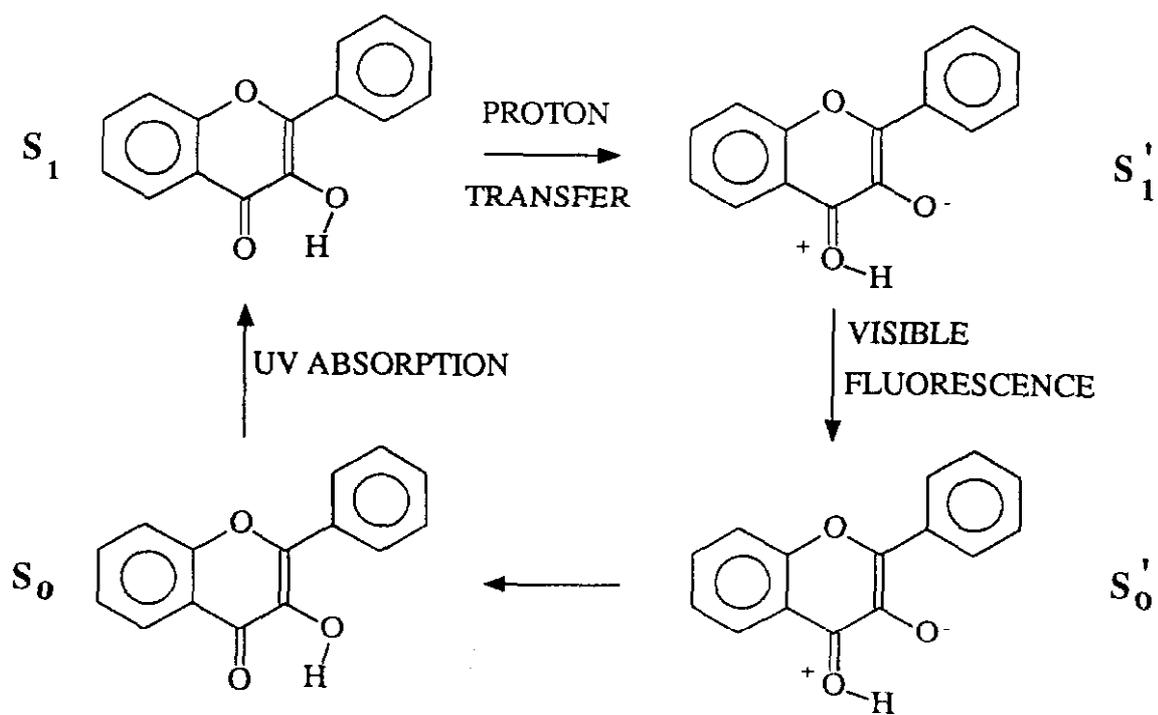


FIGURE 1

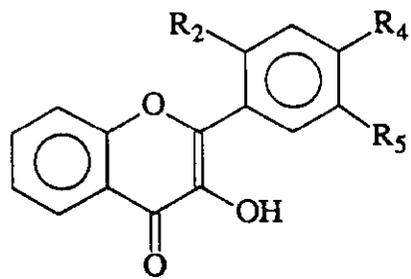


FIGURE 2

3-HF Light Yield vs. Concentration

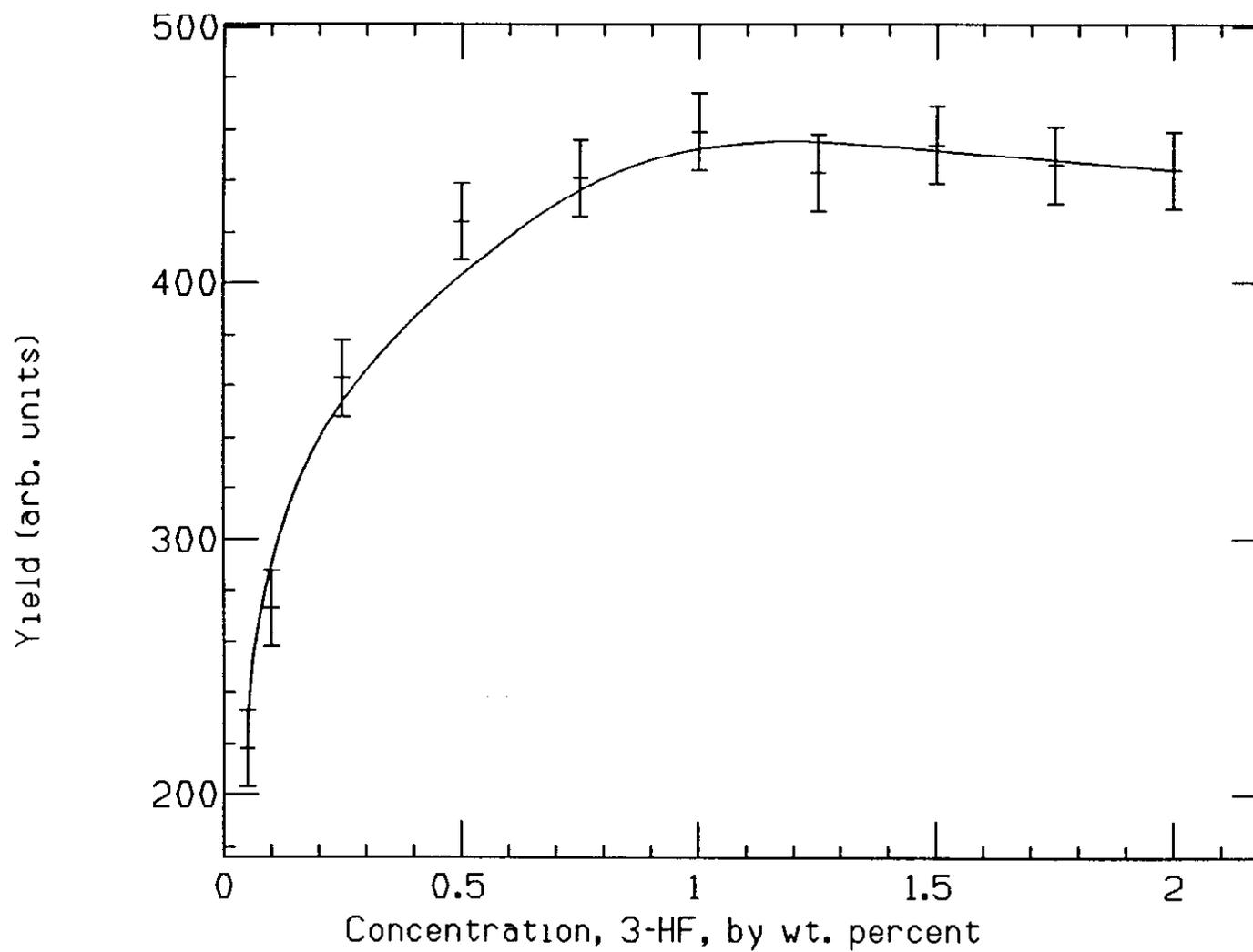


FIGURE 3

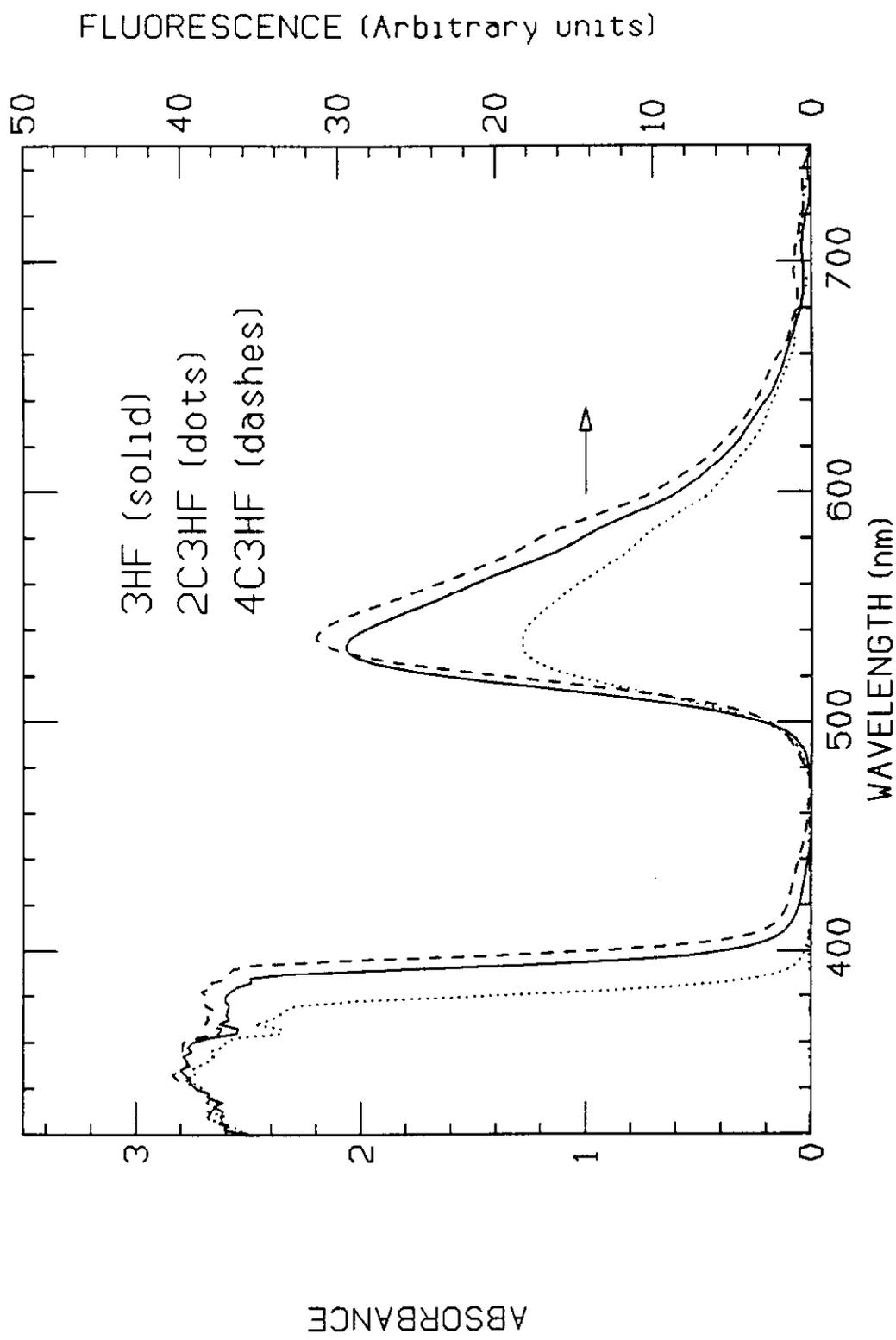


FIGURE 4

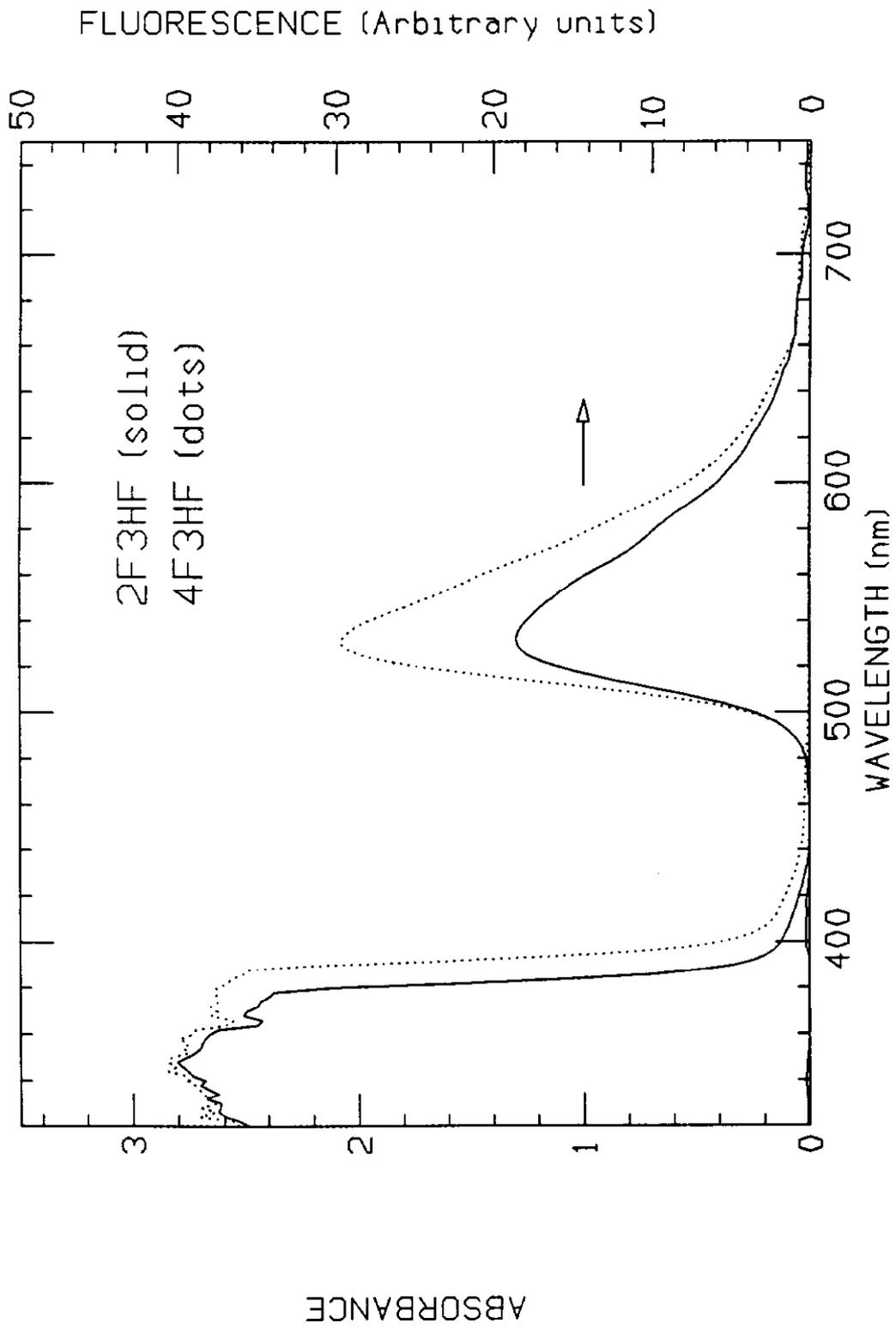


FIGURE 5

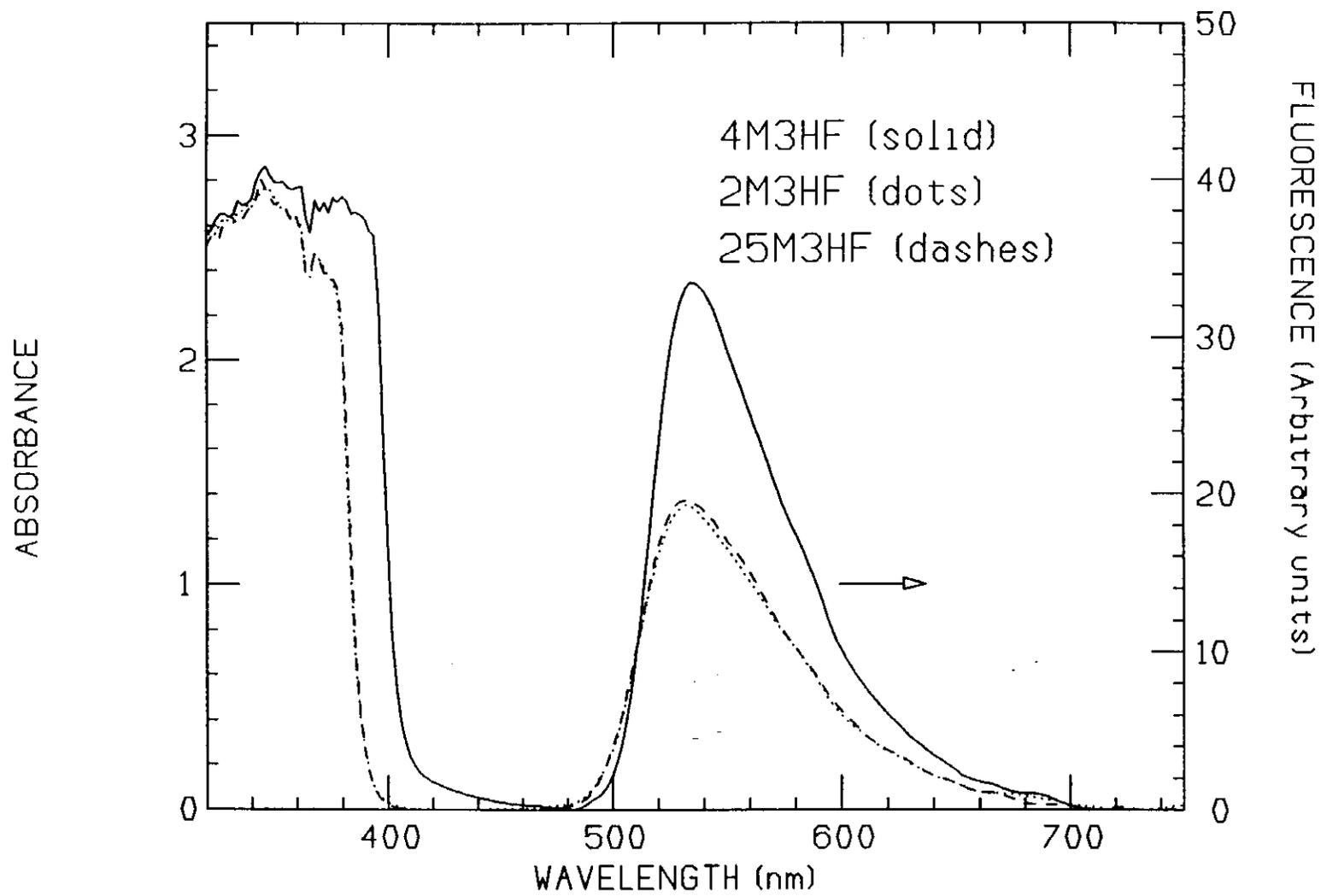


FIGURE 6

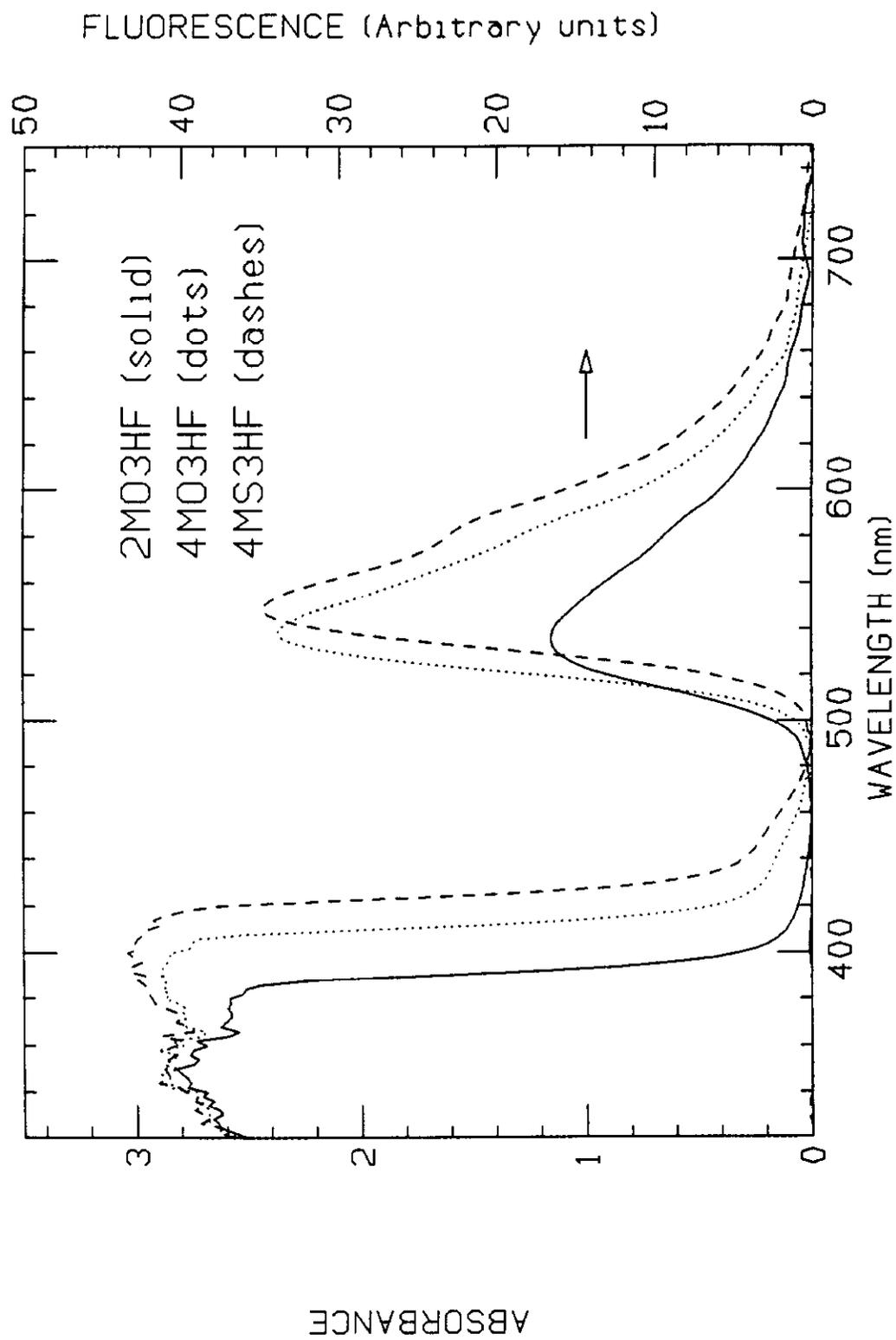


FIGURE 7

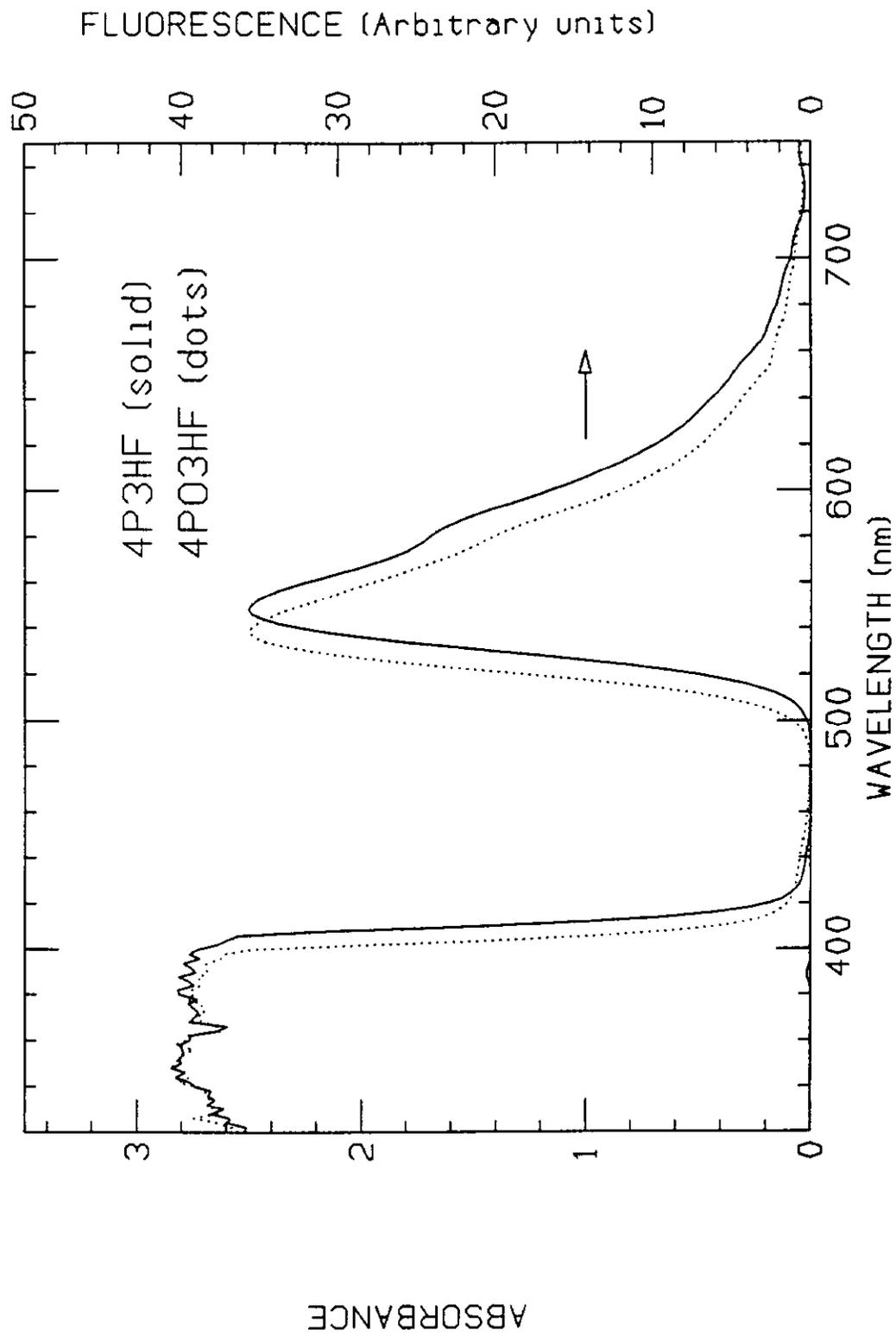


FIGURE 8

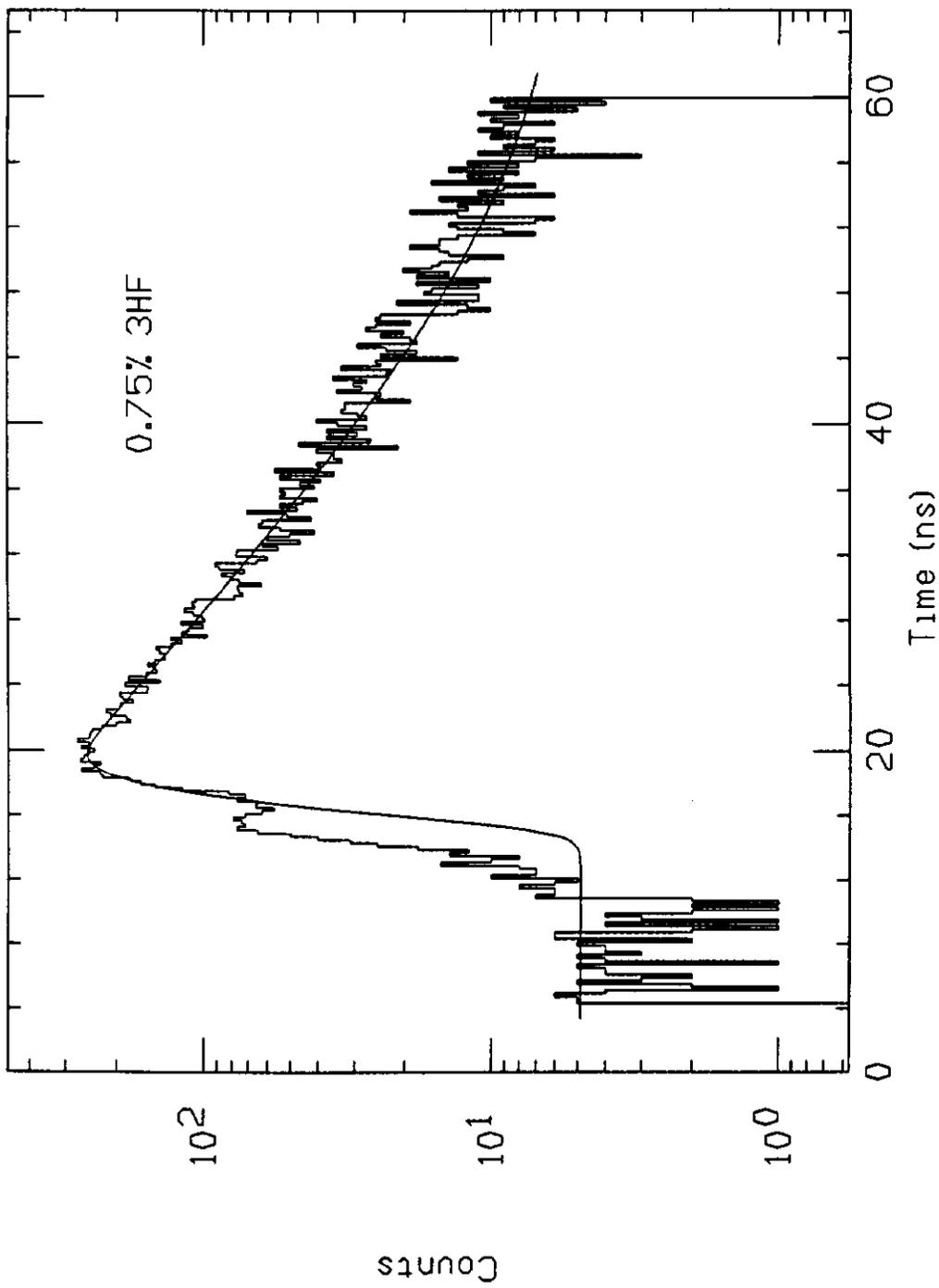


FIGURE 9

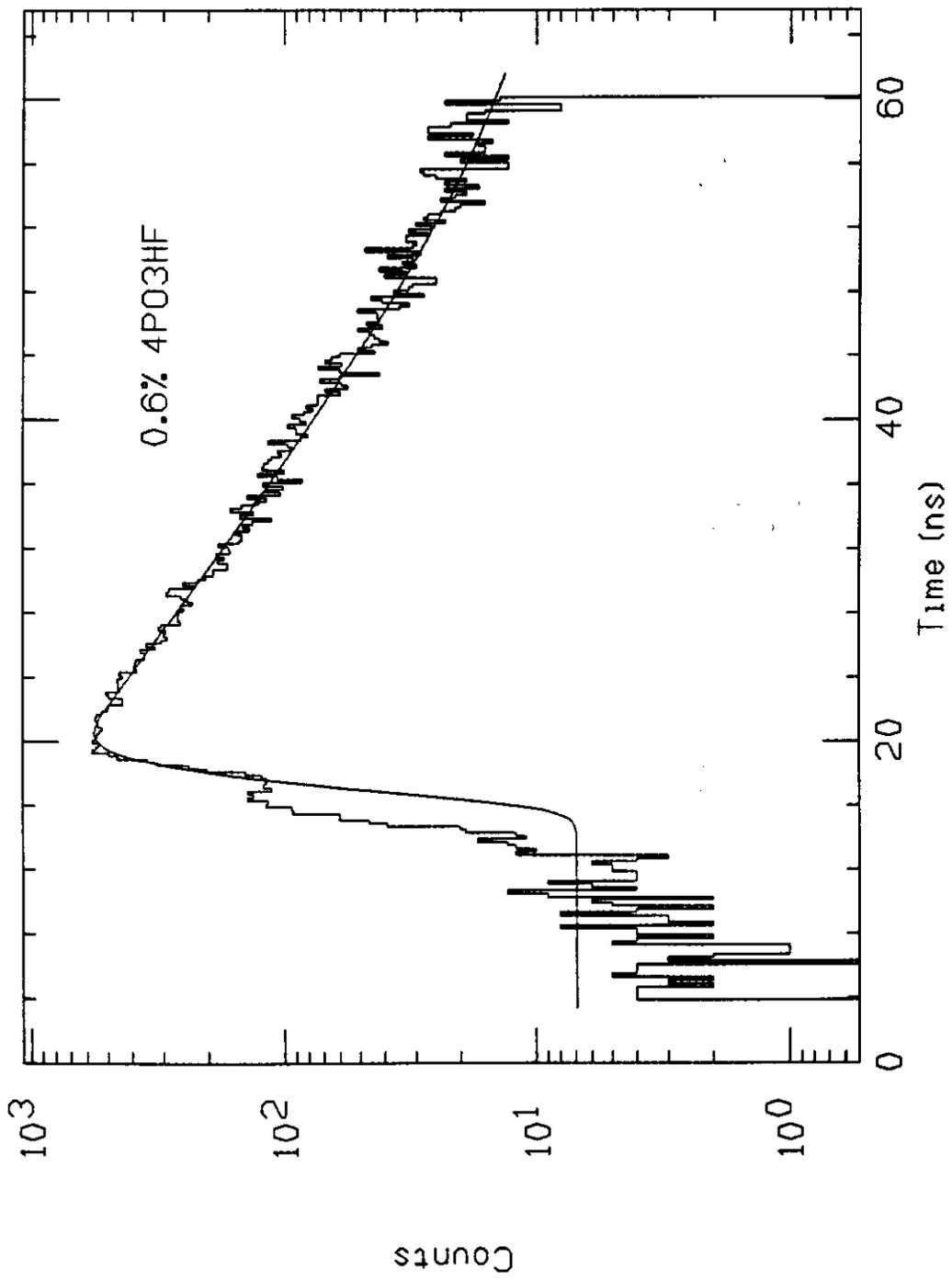


FIGURE 10