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Abstract

A series of commercially available coumarins was tested as wavelength shifters in polystyrene for a tile/fiber calorimeter application. The objective was to find a compound that when incorporated in a polystyrene matrix absorbed in the 400-450 nm wavelength range, fluoresced in the green region of the visible spectrum ($\lambda_{em}=450-550$ nm), and exhibited both short decay time and high quantum yield. Transmittance, fluorescence, and decay time determinations were performed in order to characterize each coumarin in polystyrene. Two coumarins (C510 and C515) were found to have faster decay times (~ 8 ns vs. 12 ns) and superior light output (100-120%) compared to the commonly-used green wavelength shifter, K-27.

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Introduction

Particle detectors based on inorganic and organic scintillating materials have been used in nuclear and high energy physics experiments for many years [1]. Among these materials, scintillating plastics are noteworthy for their fast response and ease of manufacture. New applications for plastic scintillation detectors have been made possible after recent developments in both scintillating plastic optical fibers and photon detection devices [2].

A scintillating tile/fiber design [3] is being built for several detectors – namely the CDF End Plug Calorimeter, the CMS Hadron Calorimeter, the ATLAS Hadron Calorimeter, and for a SDC Technical Proposal. This design consists of plastic scintillator plates embedded with a wavelength shifting (WLS) fiber which is spliced to a clear fiber. In order for this system to perform properly, the absorption spectrum of the WLS fiber must match the emission spectrum of the scintillating tile. In a number of these projects, SCSN38 (Kuraray Corp., Japan) is being considered for the scintillating tile, and BCF91 (Bicron Corp., USA) or Y11 (Kuraray Corp., Japan) for the WLS fiber [4]. SCSN38 is a blue-emitting scintillator. Both WLS fibers use K-27, a green-emitting compound, as the dopant. K-27 has a decay time of approximately 12 ns which is long in comparison to that of most blue-emitting materials (2–3 ns). Of all the factors that will affect the speed of the scintillator tile/fiber calorimeter, the lifetime of the green-emitting dopant in the WLS fiber is the dominant component. To increase the speed of the calorimeter, it would be desirable that the green WLS fibers utilized had lifetimes between 3–5 ns. However, currently available green WLS fibers exhibit decay times between 7–12 ns.

Development of new green-emitting WLS fibers with short decay times is being investigated. The goal of this project was to search for commercially available fluorescent compounds with the following specifications in a polystyrene matrix: $\lambda_{abs}=400\text{--}450$ nm, $\lambda_{em}=450\text{--}550$ nm, decay time faster than K-27 (ideally $\tau=3\text{--}7$ ns), and a quantum efficiency of a minimum of 0.7 (current K-27 baseline). Large Stokes shift and low self-absorption are not important requirements since the optical pathlength for the shifted light is small (typically 30 cm). Characterization of the spectroscopic properties of these compounds after styrene polymerization is important since this is an essential part of the manufacturing of WLS fibers. The results of the study performed on a series of commercially available coumarin derivatives and the

comparison of their spectroscopic properties with K-27 are reported here.

Experimental Section

Various coumarins meeting the absorption and fluorescence specifications listed above were purchased from Sigma, Exciton, Lambda Physics, and Eastman Kodak. Styrene was deinhibited by passage through a column filled with alumina pellets (F-200) available from ALCOA and purified by vacuum distillation. Glass polymerization tubes were treated for 10 minutes with a 30% solution of dichlorodimethylsilane in hexane in order to enable the removal of the plastic rods after polymerization. Styrene solutions were prepared containing a 0.02% (by weight) coumarin concentration. The various solutions were degassed through repeated freeze-pump-thaw cycles. The solutions were polymerized in a silicone oil bath at 125 °C for 24 hours and at 140 °C for 48 hours. The bath temperature was ramped down to 90 °C over 16 hours. After removal from the oil bath, the tubes were quenched in liquid nitrogen for a fast release of the plastic rods. The rods were cut and polished into discs of 2.2 cm diameter and 1 cm thick.

Transmittance and fluorescence spectra were recorded with a Hewlett-Packard model 8451A diode array spectrophotometer. All transmittance measurements used undoped polystyrene as the reference. The fluorescence spectra were performed using an external Hg lamp whose light was brought into the spectrophotometer by means of a quartz fiber. Different excitation wavelengths could be selected with the use of bandpass filters. Both back-surface (BS) and front-surface (FS) excitation measurements were performed. In the former, light from the quartz fiber excited the sample surface that faced away from the spectrophotometer collection optics. The sample fluorescence was thus viewed through the sample. In the front-surface (FS) excitation 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 and not through the sample. In both geometries, a 45° angle of incidence with respect to the surface plane was used.

Decay time distributions were determined utilizing a ^{106}Ru source (a β -source) which excited a SCSN38 scintillator tile which at one end was coupled to a photomultiplier tube (PMT) and provided the START signal for

a LeCroy qVt operating in time mode. The SCSN38 tile was perforated to fit and hold the green WLS sample under study (Figure 1). The WLS sample absorbed the light emitted by the scintillator and fluoresced at longer wavelengths. The geometry was such that only single photons from the WLS sample reached a second photomultiplier which generated the STOP signal. Constant fraction discriminators were used for both the START and STOP signals. A filter to remove any blue light from the scintillator was positioned in front of the STOP PMT (Figure 1). The emission time probability distribution for the WLS samples can be described by a one-exponential decay:

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

where τ_1 is the decay constant. A gaussian time error with a standard deviation σ_t was assumed, typically $\sigma_t \approx 4$ ns. The resulting time distribution is then:

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

The τ_1 parameter is determined by fitting to the data the above distribution.

Light yield measurements of the coumarin-doped WLS samples were performed using a ^{106}Ru source. This β -source excited a sample of SCSN38 scintillator holding a WLS sample. A photomultiplier tube with a green-extended bi-alkali photocathode (Hamamatsu Inc.) was utilized. The pulse height spectra were recorded with a LeCroy qVt operating in the charge mode. Light yield results reported herein are relative to K-27 and have not been corrected for the quantum efficiency variations of the photomultiplier tube over the fluorescence distribution of the coumarin sample.

Results and Discussion

Absorption, emission, and decay time data of coumarins in solution is available in the literature since they are often utilized as laser dyes [5]. This information was used for screening for compounds that approximately matched the absorption and emission wavelength range of interest for this project. However, these data contain an intrinsic drawback. The measurements are generally recorded in polar solvents such as methanol and DMSO. Because

polystyrene is not as polar as those solvents, the absorption and fluorescence spectra of the coumarins in polystyrene will likely shift towards shorter wavelengths (hypsochromic shift), and in addition, changes in the emission lifetimes will occur. The initial selection consisted of approximately 40 coumarins. This number was reduced after the compounds were tested in polystyrene. Table 1 lists the coumarins whose absorption and emission characteristics after styrene polymerization remained in the target region. Samples doped with K-27 were also prepared and characterized. They were used as the baseline in the measurements of the coumarins since the current green WLS fibers are based on K-27. Figure 2 shows the transmittance and fluorescence spectra of a polystyrene sample doped with K-27.

The coumarins studied were easily dissolved in styrene and were stable during polymerization. Samples of these dopants were evaluated after the polymerization process. Table 2 presents the spectroscopic characteristics of the coumarins and K-27 in polystyrene. Figures 3 and 4 show representative spectra of the transmittance and fluorescence data. Since the scintillating tile (SCSN38) chosen for the detector has a peak emission at 430 nm, fluorescence spectra were performed using an excitation wavelength in the same region to better reproduce the final calorimeter setup. A 436-nm excitation wavelength was utilized for these measurements. FS and BS fluorescence measurements were performed to examine self-absorption in a 1-cm path-length. Since the separation between absorption and emission spectra in the coumarin derivatives is small, there are light losses due to self-absorption. These losses are indicated by an apparent shift in the maximum of the fluorescence distribution when FS and BS emission measurements are compared (Table 2). The differences range between 2 and 14 nm, and center around 4 nm. These light losses will not affect the overall performance of the detector, because the WLS fibers are spliced to a clear fiber, and thus kept to a minimum length. Some of the coumarins (C478, C480, C487, C490, C500, and C503) outlined in Table 2 emit between 420–450 nm which is below the targeted wavelength range. These compounds fell in the borderline region and therefore were kept in the study for a full assessment of their properties. The remaining coumarins listed fluoresce in the desired area. Several coumarins show between 5–20% higher light output than K-27. Half of the coumarins tested exhibit similar or slightly lower light yield than K-27. Only four compounds have quantum yields which are 50–65% that of K-27. All coumarins show shorter decay times than K-27 ($\tau \approx 12$ ns). In some cases,

however, they are only 1-2 ns faster. A few coumarins have decay times of approximately 7 ns, but their quantum yield is among the lowest measured, rendering these compounds unsuitable for our application. C525 and C535 show lifetimes of approximately 8 ns, but their light output is only 85% that of K-27. C510 and C515 exhibit the best compromise with lifetimes of approximately between 7 and 8 ns, and light yields of 120% and 100% that of K-27, respectively.

Conclusions

Due to differences in the polarity of the solvents, the coumarins tested in polystyrene experienced hypsochromic shifts in the absorption and emission bands, in comparison to the data found in catalogs and handbooks which usually report measurements in highly polar solvents. Nevertheless, several coumarin derivatives exhibit the right spectroscopic characteristics in polystyrene and seem possible substitutes to K-27 for the green WLS fibers. Some of the coumarins studied show higher light yield (between 5–20% increase) and shorter lifetime than K-27. Among these, C510 and C515 offer the best set of properties. The coumarins analyzed represent a moderate improvement over the currently-utilized K-27. Decay times between 7 and 10 ns give rise to a minor advantage over that of K-27 ($\tau \approx 12$ ns) when the overall characteristics of the detector are evaluated.

In these applications, the WLS fibers will be used in a high-dose radiation environment. Thus, before any substitute for K-27 can be selected, the results of a radiation damage study should be considered. Such study is underway and its results will be published as they become available.

Acknowledgements

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Figure Captions

Figure 1. Scheme of the decay time determination setup.

Figure 2. Transmittance and fluorescence spectra of 0.02% K-27 in polystyrene. Excitation wavelength 436 nm, BS.

Figure 3. Transmittance and fluorescence spectra of 0.02% C510 in polystyrene. Excitation wavelength 436 nm, BS.

Figure 4. Transmittance and fluorescence spectra of 0.02% C515 in polystyrene. Excitation wavelength 436 nm, BS.

Table 1. List of coumarin derivatives included in this study.

Coumarin	CAS Registry No.	Vendor
C153	53518-18-6	Lambda Physics
C314T	113869-06-0	Eastman Kodak
C338	62669-75-4	Eastman Kodak
C35 ^a	41934-47-8	Sigma
C478	41175-45-5	Exciton
C480	41267-76-9	Exciton
C485	53518-14-2	Exciton
C487 ^b	–	Exciton
C490	53518-15-3	Exciton
C498	87331-48-4	Exciton
C500	52840-38-7	Exciton
C503	55804-70-1	Exciton
C504	55804-66-5	Exciton
C510	87349-92-6	Exciton
C515	41044-12-6	Exciton
C519	55804-65-4	Exciton
C521	55804-67-6	Exciton
C522	53518-19-7	Exciton
C523	55804-68-7	Exciton
C525	87331-47-3	Exciton
C535	27425-55-4	Exciton
C540	38215-36-0	Exciton
C545	85642-11-1	Exciton

^aC35 is equivalent to C481 from Exciton. ^bNeither the full name nor the CAS Registry number is available for this compound.

Table 2. Spectroscopic characteristics of the coumarins studied.

Dopant ^a	Cutoff ^b (nm)	FS Emission ^c (nm)	BS Emission ^d (nm)	Lifetime ^e (ns)	L. Yield ^f (%)
K-27	480	468,496,530	496,530	11.8	100
C153	470	478	480	10.8	99
C314T	460	456	468	9.6	106
C338	460	460	472	9.7	105
C35	450	456	460	9.1	95
C478	420	422	428	6.9	65
C480	430	424	428	7.2	63
C485	450	452	456	9.3	107
C487	420	426	430	7.2	62
C490	420	426	430	6.9	52
C498	470	456	470	9.5	109
C500	440	440	444	8.0	85
C503	440	442	446	8.1	88
C504	470	458	468	8.5	-
C510	480	478	484	7.6	119
C515	480	478	492	7.5	100
C519	490	474	488	10.0	100
C521	490	476	490	10.3	106
C522	460	466	472	9.4	113
C523	490	470	484	10.0	95
C525	520	508	518	8.1	82
C535	500	504	508	7.7	85
C540	510	510	514	7.4	90
C545	520	526	528	8.4	76

^aConcentration of dopant in polystyrene is 0.02% by weight. ^bAbsorption threshold for 1-cm thick samples. ^cEmission spectrum using Front Surface excitation, $\lambda_{exc}=436$ nm. ^dEmission spectrum using Back Surface excitation, $\lambda_{exc}=436$ nm. ^eEstimated measurement error is of ± 0.2 ns. ^fLight yield results are relative to K-27, when being used as WLS under side illumination by a sample of SCSN38 scintillator, viewed by a green-extended bi-alkali PMT.

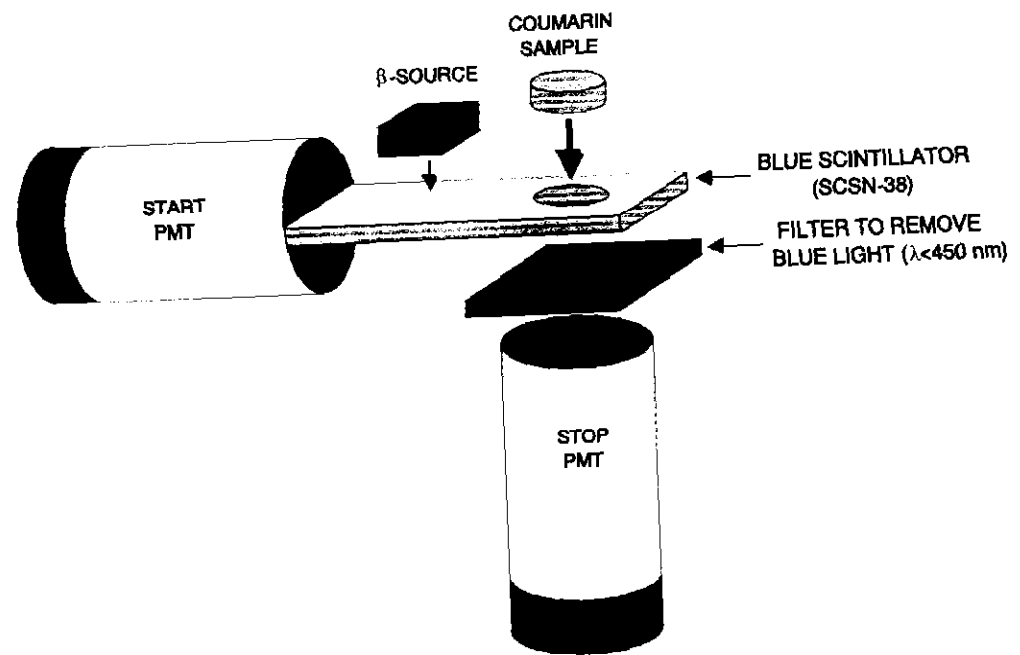


FIGURE 1

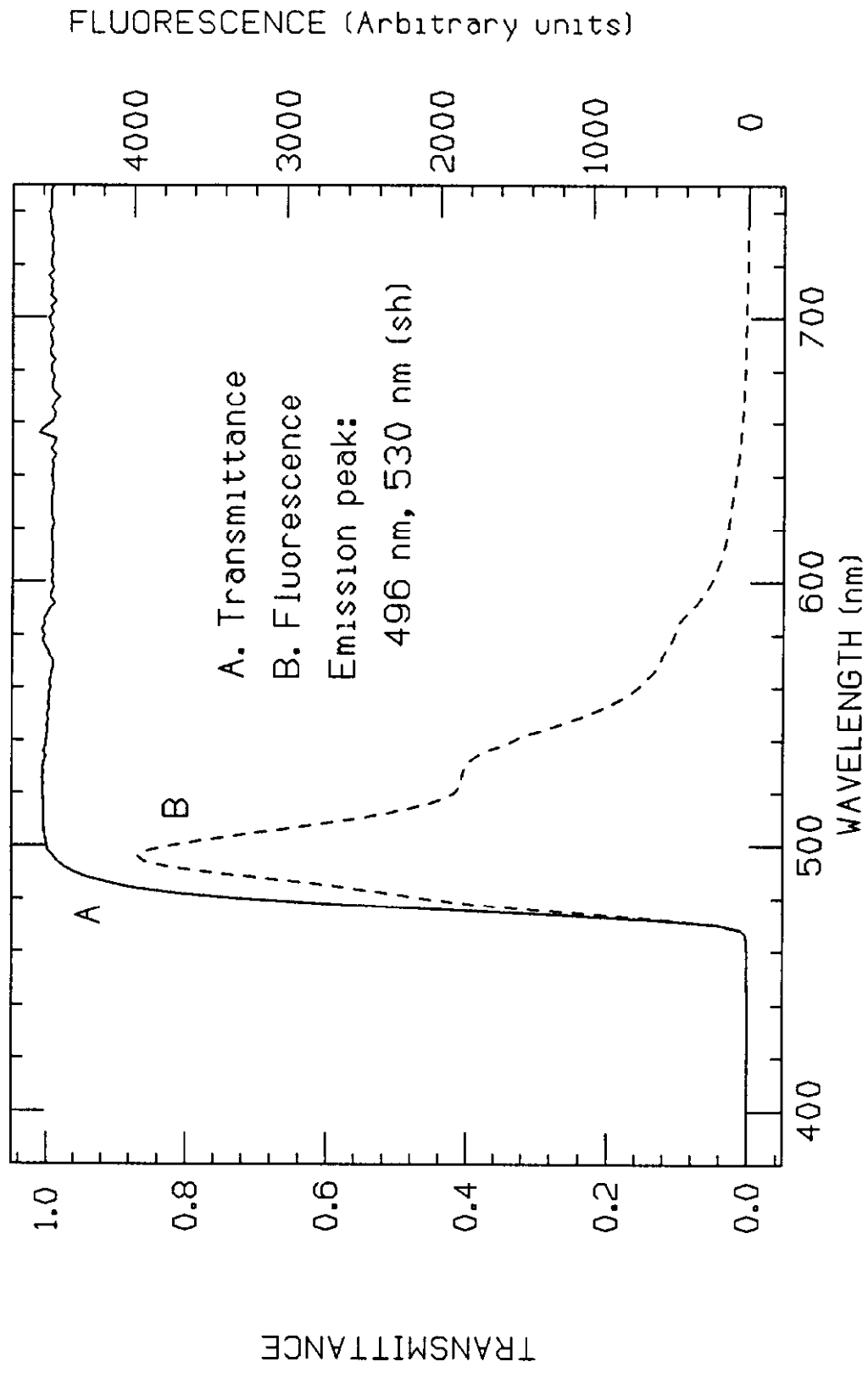


FIGURE 2

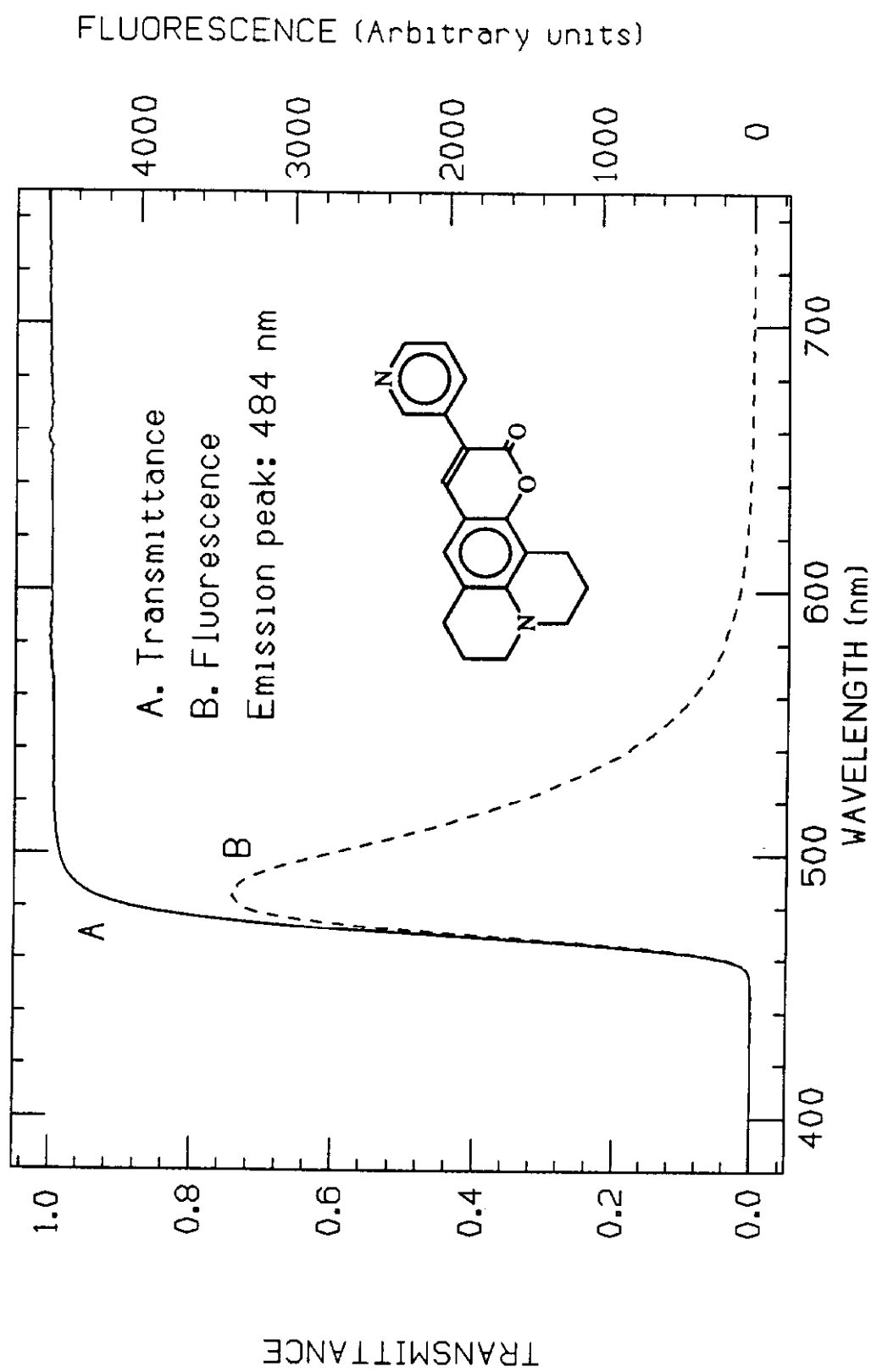


FIGURE 3

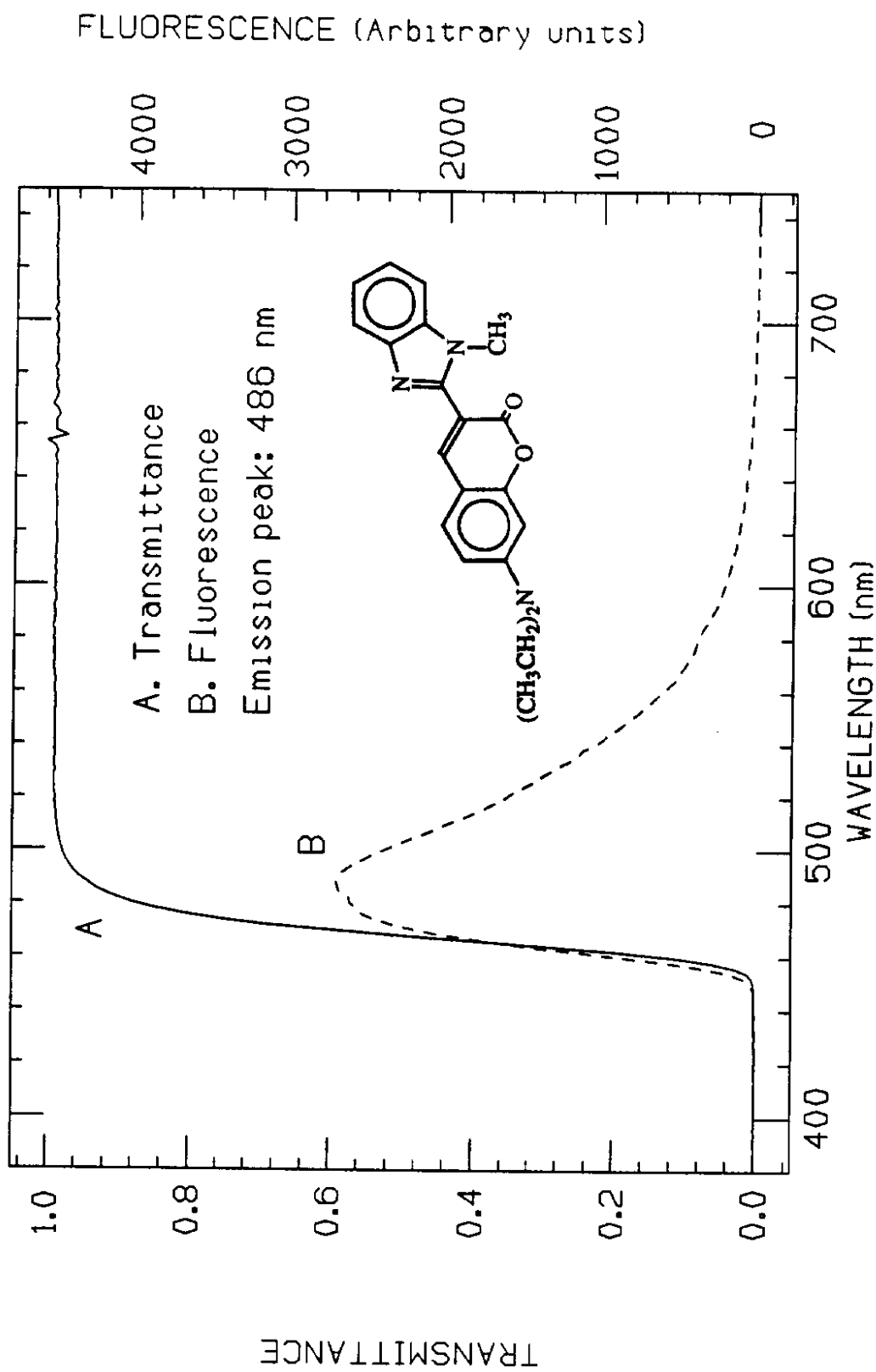


FIGURE 4