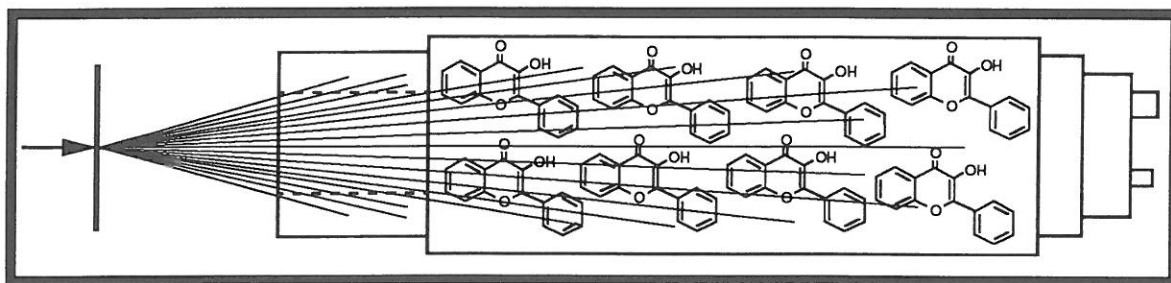


Proceedings of the

Workshop on Radiation Hardness of Plastic Scintillator



March 19-21, 1990
Florida State University, Tallahassee, Florida

Editor
Kurtis F. Johnson

PREFACE

The Workshop on Radiation Hardness of Plastic Scintillator was held at Florida State University, in Tallahassee, from March 19 to March 21, 1990. The emphasis was on gathering the most current data on the degrading effects of radiation on plastic scintillator, and the consequential impairment of calorimeter resolution and energy calibration. Results of both measurements and monte-carlo experiments on radiation damage to calorimeters were presented.

Nearly an entire day of presentations was devoted to the chemistry of polymers and fluors. After an introduction by Adam Para (Fermilab), who presented an overview of the opportunities and technical difficulties which the SSC presents for detector development, several distinguished chemists spoke on various aspects of radiation damage to plastic scintillators. Roger Clough (Sandia) described their program of systematic search for possible rad-hard bases and new useful fluors. Joel Kauffman (PCP) described progress in designing new, rad-hard fluors of the oligophenylene and pyrazoline families and large Stokes-shift derivatives of POPOP. James Walker (UF) described his group's work in fabricating rad-hard polysiloxane-based scintillators. Mike Kasha (FSU) discussed the molecular electronic criteria of rad-hard scintillator dyes.

There were also a series of presentations of recent data. Carl Zorn (CEBAF) presented new data from his group and reviewed extensively and clearly the damage phenomena and many of the recent advances in hardening scintillators. Amelia Maio (LIP) gave an expansive and detailed overview of the ongoing program of fiber measurements in Lisbon. And Kiyoshi Yasuoka (TU) released quantities of new data on fiber measurements in various atmospheres.

Monte Carlo investigation of many aspects of the SSC (possibly including the financing!) will be essential until the beams are switched on, and beyond. Radiation damage to detectors is no exception to this, so we were fortunate in having Don Groom (LBL) as a participant to drive home how truly ferocious the radiation field in the interaction regions are going to be, and to put the albedo neutron problem into perspective.

Jean Badier (EP) showed the results of his analytic/monte-carlo investigation into the effects of radiation on the performance of a fiber calorimeter. Tony Gabriel (ORNL) and Tom Handler (UT) proffered the conclusions of their monte-carlo study of plate calorimeters.

Monte-carlo investigations are certainly necessary but are just as certainly insufficient. Real-life beam tests of assembled units are necessary to ferret out any unexpected synergistic effects, but real-live test beams are in very short supply. Stan Majewski (CEBAF) launched a barrage of observations and suggestions on the shortage of high-energy test beams and how to circumvent it. Bill Dunn (QRS) revealed the inner ducting of his PULSTAR reactor and his scheme to use it for neutron damage tests.

Jimmy Proudfoot (ANL) shared his conviction that a lack of complete resistance to radiation damage should be considered a design criterion and provided an example. Bill Worstell (BU) showed us how to manufacture fiber calorimeters in an oxygen-free environment.

Dave Hertzog (UIUC) presented an update on one of the very few attempts to systematically measure radiation damage of a calorimeter.

Finally, Nikos Giokaris, (RU) opened our eyes as to how very limited our understanding of radiation damage phenomena is, with his report of severe long-term, very low dose damage to the CDF beam-beam counters.

In addition to the individual presentations, there were also two round table discussions, during which the audience was able to indulge its naiveté in a less formal setting and ask for details on the "best-guess" judgements of the experts.

Finally, the chairmen would like to thank all those who contributed to the organization of the Workshop, including the members of the Local Organizing Committee, L. Dennis, V. Hagopian and H. Wahl, as well as the FSU staff, S. Beasley, L. Knudsen and K. Mork.

K. F. Johnson
A. Para

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DESIGNING A RADIATION-HARD PLASTIC SCINTILLATOR FOR HIGH LUMINOSITY HADRON COLLIDERS

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ABSTRACT

The planned construction of the SSC and LHC facilities have created a resurgence of interest in the damaging effects of radiation upon active detector components. This paper is a discussion of recent research into improving the radiation tolerance of plastic scintillators, with specific reference to their use in the form of scintillating optical fibers.

I Introduction

Simulations of the ambient radiation environment for detectors at the planned SSC and LHC facilities have shown that many of the commonly used detector elements will endure damaging levels of radiation from the interaction regions. Plastic scintillators are often used, especially as the sampling element in calorimeters. The phenomenology of high energy, high luminosity hadron collider physics has led to the importance of calorimeters as key elements in the analysis of the underlying physics. The classical method of detection, that is, the sampling of a shower of ionizing particles, will result in degradation of the scintillator performance (the standard sampling element), with the consequent overall loss of calorimeter performance, especially in the all-important aspect of energy resolution. Radiation levels in excess of 10^4 Gy/yr can be expected in the forward parts of the calorimeters. Standard commercial plastic scintillators are known to suffer significant changes in performance at such radiation levels.

A standard calorimeter design consists of a sandwich of high-Z material (e.g., lead, steel) alternated with sheets of plastic scintillator. Within the past few years, there has been an growing interest in using the plastic scintillator in the form of optical fibers: a central core of doped polystyrene (PS) (with a typical diameter of 1 mm) surrounded by a lower refractive index cladding (PMMA is the standard choice) of several microns thickness. For a variety of reasons [1], a high Z material with embedded scintillating fibers is being seriously proposed as a possible calorimeter design for the SSC and LHC.

Scintillating fibers are also being proposed for use as central tracking elements [1]. In this case, the radiation levels are not expected to be as severe, but they will still require a good level of tolerance to radiation. More importantly, they will require good attenuation lengths and high light output. As will be shown in this paper, the improvement of radiation resistance may result in a significant increase in attenuation length. Prudent choice of the dopant fluor may also result in a brighter scintillator.

Research into the problem has resulted in significant strides towards producing a plastic scintillator suitable for the hadron collider environment. Although the problem of

producing radiation-hard plastic scintillators has not been finally resolved, research in the last few years has been sufficient to allow one to (a) propose and test preliminary solutions to the problem, (b) define most of the remaining problems, and (c) for the most part, determine the method of resolving the problems. This paper will be a discussion of the nature of the problem and how one hopes to finally resolve it. Reference [2] can provide the interested reader with additional references on the subject.

II Radiation Damage Phenomenology

Irradiation of plastic scintillator results in two classes of optically observable damage: (I) a change in the attenuation characteristic of the scintillator, and (II) a loss in light output independent of any attenuation changes. Class I has been mostly attributed to the increased UV and blue absorption induced in the plastic base but may have contributions from degradation products of the dopant fluors, as well as from other additives used in the manufacture of the plastic. Class II is due to either direct damage to the fluor(s) or to an interference of the energy transfer between primary and waveshifter fluors (although this latter effect is actually attributable to the induced UV absorption in the plastic at the wavelengths where the energy transfer takes effect, that is, a Class I effect producing Class II).

The direct degradation of the fluors is still under study, but results presented at this workshop [3] indicate that in oxygen-free conditions, several commonly used (or interesting) fluors show considerable levels of resistance to damage even after a 100 Mrad dose: PTP - 100% survival, 3HF - 78%, and BPBD - 67%. There are also some with perhaps unsatisfactory levels of resistance: TPB - 58%, POPOP - 44%, PMP - 35%, and rubrene - 26%. It is important to point out that studies in an oxygenated atmosphere will be required as this may affect the resistance levels drastically.

The effects of oxygen brings us to an important issue. Due to the large doses needed for the experimental evaluations (minimum of 1 Mrad usually), it is necessary to utilize high dose rates (50-1000 krad/hr is typical). Under such a condition, one observes annealing behavior in the scintillator. This is certainly a Class I phenomenon, although there may be a Class II component as well. Figure 1 shows this phenomenon in terms of transmission changes observed through 1 cm of plastic scintillator. Immediately after the high dose rate irradiation (to a specified total dose), a large change in transmission is observed. In an oxygenated atmosphere, a relatively rapid improvement in transmission is observed to occur which achieves a plateau at some permanent residual level of damage (which is a function of the total absorbed dose). This is observed as a steady bleaching of the plastic, starting at the surface, and progressing inward at a rate which corresponds to the diffusion rate of oxygen in the plastic (for the given atmospheric oxygen concentration) [4,5]. For the sample in an inert atmosphere (argon), the rate of recovery is much slower. It is generally believed that small contaminant levels of oxygen are probably responsible for the observed recovery.

It is natural to ask if the permanent residual damage would be the only damage observed if an appropriately low dose rate exposure was made (to the same integrated dose). Such an experiment [4,5] has been made with 3 mm thick sheets of the polystyrene-based

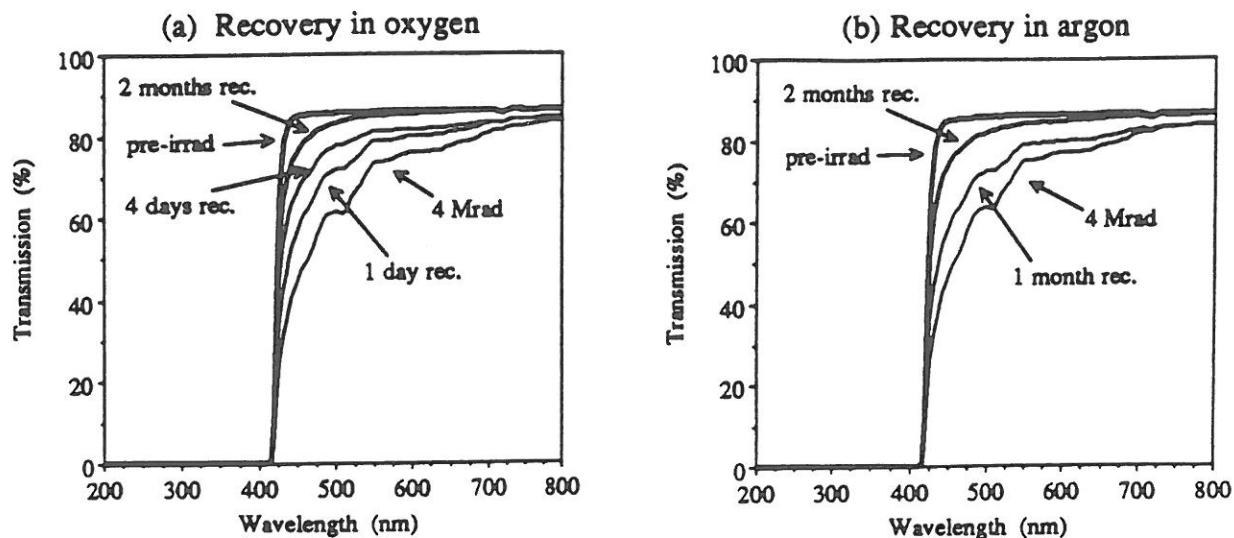


Figure 1: The effect of oxygen upon the recovery (in transmission) of two samples of a plastic scintillator (right-circular cylinders 1 cm thick and 1.5 cm diameter). It is assumed that the recovery seen in argon is probably due to contaminant levels of oxygen being present.

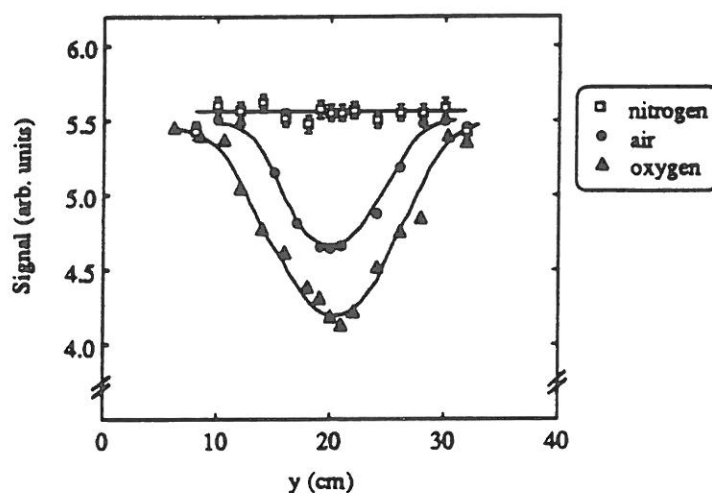


Figure 2: From reference [6], a low dose rate (10 rad/hr to a total dose of 11.5 krad by a 7 mC ^{90}Sr source) exposure of PMMA-based scintillators in different atmospheres indicates the strong effect of oxygen which can diffuse into the plastic during irradiation. It remains to be seen whether a similar effect is seen for polystyrene and PVT based scintillators. The current data indicate that PMMA recovers slowly (in oxygen) while polystyrene and PVT recover rapidly. This recovery reaction may prevent the occurrence of the effect presented in figure 2. The graph presents the change in relative scintillation output across the length of the scintillator sheet relative to pre-irradiation.

scintillator SCSN-38 for the following conditions: dose rates ranging from 3 krad/hr to 1 Mrad/hr, a total dose of 2.5 Mrad, and the irradiation and recovery performed in air. The results indicated that after annealing, the level of permanent damage was identical for all dose rates. In addition, annealing during irradiation was indicated as the immediate post-irradiation damage decreased as the dose rate was lessened. In fact, the data indicated that for dose rates below 4.5 krad/hr, the annealing reaction counteracted any additional damage (beyond that of the permanent residual level). It is important to note the conditions: (1) the 3 mm thickness of the scintillator, (2) the fact that the base plastic was polystyrene, (3) the concentration of oxygen (20% at 1 atmosphere pressure and normal temperature), and (4) the possible effect of the dopant fluors. (From studies with other scintillators and waveshifters, the researchers noted a dependence of recovery rate as a function of dopants.)

It appears from this that it may be possible to directly correlate the results of high dose rate experiments with what is expected at realistic low dose rates. This may be so, but there is other evidence that, at the very least, a check must be made of the effect of oxygen at very low dose rates. One study [6] of a PMMA-based scintillator has shown that oxygen is highly damaging at a low dose rate (10 rad/hr) (figure 2). Since high dose rate experiments indicate that PMMA is radiation-soft relative to polystyrene [4,5], then it may be that oxygen may simply be far more damaging to PMMA than to polystyrene. Another study [7] found that oxygen may have damaging post-irradiation effects after a typical high dose rate irradiation (70 krad/hr). Figure 3 shows the recovery in the relative scintillation signal for two samples of a PVT-based scintillator, one recovered in argon and the other in oxygen. To increase the rate of recovery, the ambient temperature was raised to 50°C. Although the sample in oxygen recovered faster, its plateau was at a level considerably below that of the sample recovered in argon. If the concentration is a controlling factor, then it may be that oxygen can increase the final residual level of damage. Alternatively, the effect could be an enhancement caused by the increased ambient temperature. That is, at normal room temperature, no such effect may occur. In any case, the point of both studies is made: the role of oxygen at more realistic dose rates must be checked so as to avoid any additional damage that may be produced by diffusing oxygen during irradiation.

III Radiation Hardening of Plastic Scintillator

(a) Waveshifting

In order to develop a scheme for radiation-hardening of the scintillator, it is necessary to have some understanding of the process known as scintillation. In general, the process is highly complex [8], but the essential features are simple to comprehend. In a fundamental sense, the purpose of a scintillator is to act as an energy convertor: some energy from an ionizing particle is sampled, and through a series of energy transfers (and degradations), some of this energy is output as detectable light. The common base plastics (polystyrene (PS) and polyvinyltoluene (PVT)) are themselves weak fluorescent emitters with absorption and emission bands (in the deep UV). By doping the plastic with an efficient fluor whose absorption band matches the emission of the plastic, energy can be transferred from the plastic to the fluor. At low concentrations, the transfer is radiative. By increasing

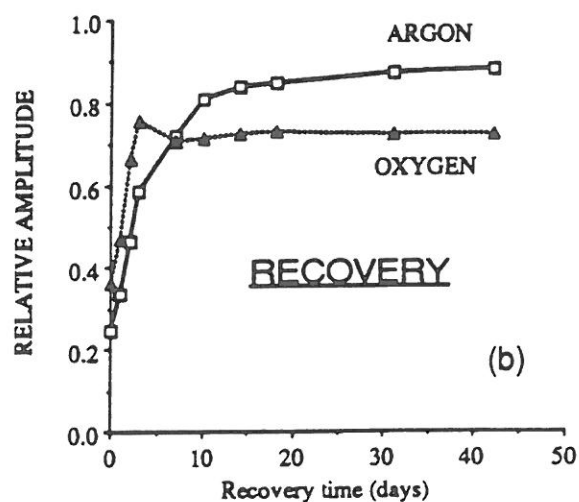


Figure 3: The recovery (in oxygen and an inert atmosphere) in the relative scintillation pulse height for two identical scintillator samples (as in figure 1) after receiving identical irradiations (6 Mrad from ^{60}Co source at 70 krad/hr). To enhance the rate of recovery, the ambient temperature was raised to 50°C . The result is somewhat in contrast to that shown in figure 1 where it is seen that oxygen results in the rapid recovery of transmission. Reference [4] notes similar contrasting results between scintillation and transmission.

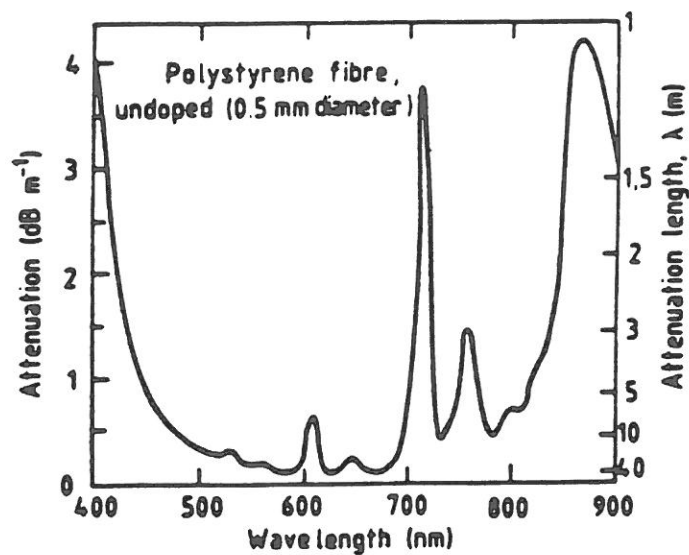


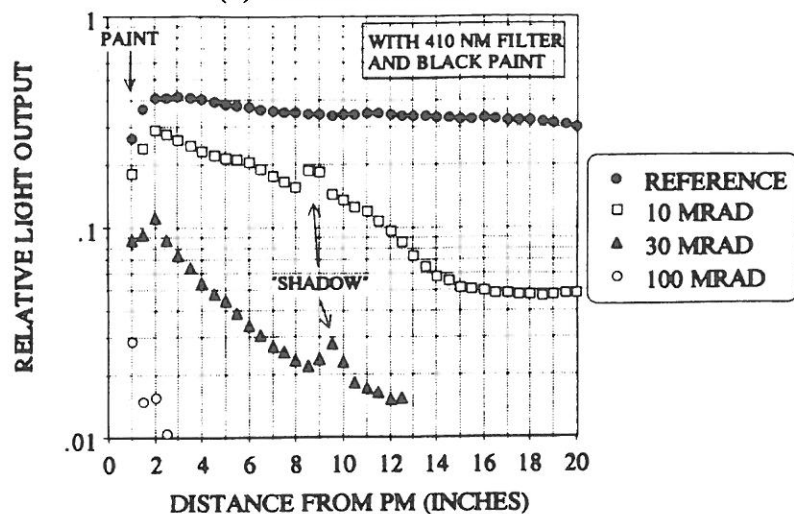
Figure 4: The attenuation characteristic of a polystyrene fiber. This result is taken from reference [22].

the concentration, the mode of transfer becomes dominated by a fast, Coulombic, non-radiative transfer mode known as Förster transfer [9]. The increase in concentration results in higher light output and a faster scintillator. Self-absorption by the fluor (caused by the residual absorption in the emission band of the fluor) will limit the final light output level (assuming solubility does not limit it first.) Typical primary fluors (e.g., PTP) emit in the higher UV (360 nm) which would be preferentially absorbed in the plastic base. (In addition, PMTs would require an expensive UV-transmitting faceplate for efficient detection.) To avoid these problems, a secondary fluor is added, whose absorption matches the emission of the primary. Self-absorption limits the concentration level with the result that the mode of transfer is radiative. With this basic knowledge of scintillation and damage phenomenology, one can propose a method for radiation-hardening of the plastic scintillator.

If one assumes that for integrated doses below 10 Mrad fluor degradation is minimal, then it is clear that the chief problem lies in the Class I phenomenon of additional induced absorption below 450 nm (increasing dramatically below 400 nm) which can (a) absorb the final emitted light, but whose major effect is (b) the interference of the radiative transfer between the primary and secondary fluors. The ideal solution to this problem would be to utilize a single, efficient, soluble, UV-absorbing, large Stokes shift fluor which non-radiatively absorbs energy in the UV and emits it at wavelengths above 500 nm. It is assumed that such a fluor displays significant tolerance to irradiation, and that it has sufficiently small residual absorption in its emission band. (This latter aspect determines the macroscopic attenuation properties of the scintillator.) As an alternative to such a case, one could also have a system with a primary fluor having as large a Stokes shift as possible (to escape the most significant absorption band induced in the plastic) followed by an additional waveshifter to the longer wavelengths above 500 nm. The macroscopic absorption properties of the base plastic (usually polystyrene) can suggest a preferred final wavelength (figure 4). The wavelengths where minimal absorption occurs are at about 550 nm (green) and 650 nm (red). A boundary condition can be set by the fact that present day photodetectors are inefficient for the red wavelengths. In addition, although enhanced green-sensitive phototubes are better in overall efficiency than regular blue-sensitive bialkali tubes in the green region (500-550 nm) [10], the difference may not be great enough to justify the additional cost of the former. Hence it may be better to aim for optimum performance at the green wavelengths with standard bialkali PMTs as the photodetector. Large improvements in developing efficient green- and red-sensitive photodetectors (e.g., APDs and SSPMs) may change that conclusion several years from now.

To illustrate this principle of waveshifting, we refer to figure 5. These are measured attenuation curves for a number of 1 mm diameter scintillating fibers (polystyrene core, PMMA cladding). All were irradiated to several doses via a 3 MeV scanning electron beam in an accelerated test (typically 1-10 Mrad/hr). To eliminate any oxygen effects during irradiation, an inert gas (argon) was flowed over the fibers during irradiation. Recovery was allowed to take place in air over a period of 2 weeks. Figures 5(a)-(c) displays the results for a blue, green, and red fiber, respectively. Both fibers from figures 5(b) & (c) utilize 3HF, a large Stokes shift fluor, to absorb energy in the UV and emit in the green. The red fiber uses an additional waveshifter to move the final emission to the red.

(a) BLUE FIBER



(b) GREEN FIBER

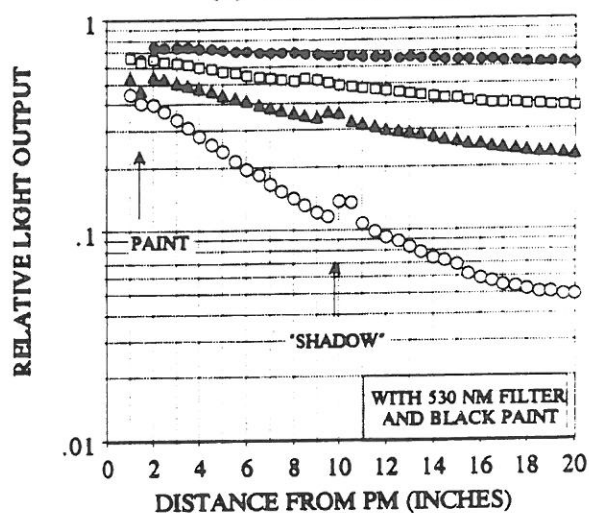
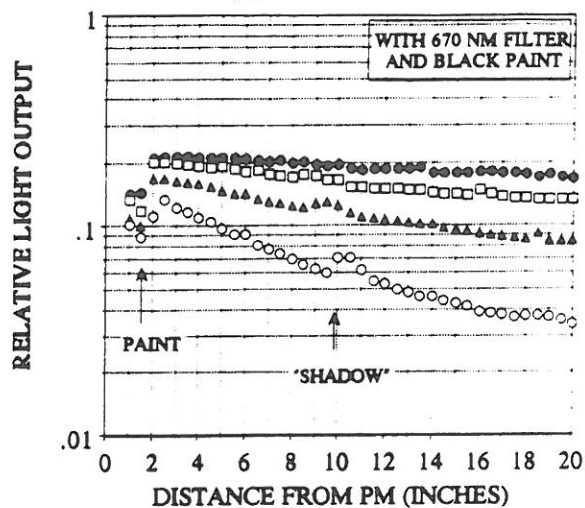


Figure 5: A demonstration of increasing the radiation tolerance of plastic scintillating fiber by shifting the emission out to longer wavelengths. As the emission wavelength is shifted to longer wavelengths, the change in attenuation length (as a function of dose) decreases. The "shadow" region is a portion of the fiber that was shielded from irradiation for the purpose of determining the intrinsic scintillation loss (see figure 7). The fibers were subjected to a typical accelerated test: high dose rate irradiation (10-30 Mrad/hr) in an inert atmosphere (argon) followed by 2 weeks of recovery in air. Note that only attenuation changes are presented here—the measurements were normalized to the PMT end of the fiber.

(c) RED FIBER



A technicality must be noted here concerning attenuation measurements of fibers. Figure 6 shows the attenuation curve of a typical unirradiated blue-emitting fiber. Note the multi-exponential character of the curve. A group at Caltech [11] has shown conclusively that most of this deviation from a simple exponential is due to cladding light that is able to propagate into the phototube. When a one-inch long layer of black paint is applied (on the outer surface of the fiber) 1 cm from the PMT end of the fiber, most of this behavior is cancelled. The small level of non-linearity is most likely due to preferential absorption of the blue end of the fluorescence spectrum by the plastic at longer distances from the PMT. This seems to be so as the use of the blue filter (410 nm) produces a clean, simple exponential as figure 6 shows.

As a further technical point, one should note that the absorption band for 3HF does not match well with polystyrene. Unfortunately a major part of the absorption band is not deep enough in the UV. However this remaining part matches very well with the emission band of the standard primary fluor PTP. Use of the primary fluor results in a much brighter scintillator. Hence, in some sense, 3HF is partially a waveshifter to PTP. However, one can increase the concentration of the 3HF so as to obtain a condition of non-radiative transfer between the PS/PTP and 3HF. This should produce a higher level of radiation resistance although it may also decrease the attenuation length of the fiber due to self-absorption by the 3HF. Figure 7 displays the irradiation results for three fibers in which the PTP concentration was held constant and the 3HF concentration was varied. During the irradiation, a small portion of the fiber was shielded from the electron beam to leave it virgin. The resultant step size produces a figure of merit as to how much damage is done to the *intrinsic* scintillation output: the larger the step size, the greater the damage. Figure 7 shows quite clearly the advantages of increasing the 3HF concentration. As far as attenuation is affected, figure 8 compares two unirradiated fibers whose only difference is a factor of 10 in the 3HF concentration. The decrease in attenuation at the higher concentration is noticable but not catastrophically different.

The improvement in radiation resistance with respect to intrinsic scintillation damage (Class II) can be attributed to two effects: (1) the effect of non-radiative transfer bypassing the induced absorption in the plastic, and (2) the effect of being on the plateau of light output. The latter requires further explanation. As the concentration of 3HF is increased, the total light output becomes limited by self-absorption from the residual absorption in the emission band. Assuming a plateau is reached, then for a sufficiently high concentration, some level of damage to the fluor will still result in enough fluor left to produce only a small loss in light output. This, of course, assumes that the damaged 3HF does not significantly contribute additional absorption centers. Recently obtained data [3] indicates that this in fact may happen. The first effect follows from the phenomenology of radiation effects and the physics of scintillation. The second effect will require some level of experimental verification so that a relative measure of the two effects can be determined.

(b) Alternative Plastic Bases

Another approach to improving radiation resistance would be through improving the radiation resistance of the base plastic itself. Some recent research has indicated the

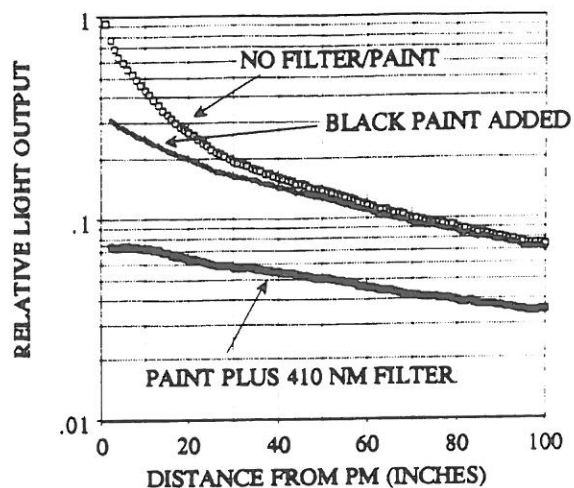


Figure 6: The effect of cladding light upon the attenuation curve can be eliminated by applying an extramural absorber (in this case, a one-inch long layer of black paint one cm from the PMT end of the fiber). An appropriate filter can eliminate the remaining effect due to short-wavelength absorption by the plastic.

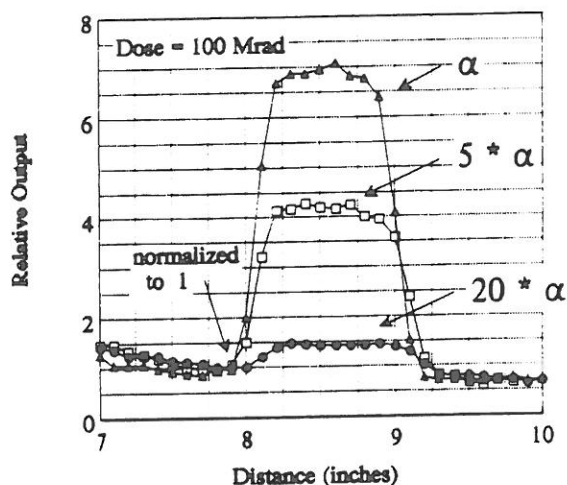


Figure 7: The effect of the concentration α of the fluor 3HF upon the loss in intrinsic scintillation yield after irradiation (and recovery). A portion of the fiber was protected from irradiation by use of a lead shield. The size of the step between the irradiated and virgin section of the fiber gives a figure of merit: the larger the step, the larger the loss in intrinsic scintillation yield.

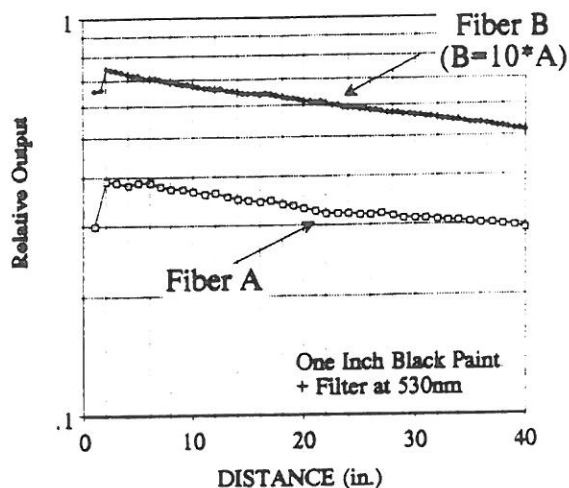


Figure 8: The effect of 3HF concentration upon the attenuation curve of the fiber. Fiber B uses 10 times the concentration of 3HF doped in fiber A.

possibility of poly-(α -methyl)-styrene as a possibly more radiation-hard base [3]. There is also a result from a number of years ago [12] that indicates promise in polyvinylxylene as a radiation-hard replacement for polystyrene and polyvinyltoluene. However, there seem to be severe manufacturing and mechanical difficulties with this material [13]. There are also some interesting results with the polysiloxane family [14]. Unfortunately, there is a large body of work required before this material can be properly evaluated alongside PS-based and PVT-based scintillators (e.g., no standardized polysiloxane scintillator fiber or plate samples are available for independent evaluations). The initial results seem promising with the prominent case of one scintillator sample (a 1.5 cm³ cube) showing no observable damage after a 30 Mrad exposure. Care must be taken with interpreting this result. First, this test was carried out in an inert atmosphere, taking advantage of the much larger porosity of the polysiloxane to oxygen as compared to polystyrene. (In fact, the replacement of oxygen with an inert gas within this plastic may be an indication of the effect of dissolved oxygen upon permanent residual damage in PS and PVT.) There is data from a previous study [15] of polysiloxane that indicates that the presence of oxygen will strongly affect the irradiation results even at high dose rates. As stressed previously, the effect of oxygen must be accounted for in evaluating a scintillator. Secondly, an early test of 3HF doped in polystyrene [7] showed that this 1 cm thick sample recovered *fully* after a 10 Mrad exposure. Clearly this behavior could not be extrapolated to the case of real fibers of a meter or more in length.

It should also be noted that in comparing the absorption changes in the polysiloxane to those in polystyrene and polyvinyltoluene, only the immediate post-irradiation results have been displayed. This is an incorrect comparison as the present body of evidence indicates that the post-annealing residual damage (which is much smaller than the post-irradiation damage) in polystyrene is the actual level of damage that would be observed at realistic dose rates [4,5]. As yet, no annealing behavior has been presented for polysiloxane. In other words, the differences between polysiloxane and polystyrene are not so large as they first appear. Here again, the irradiation of the polysiloxane was performed in an inert atmosphere. Any possible deleterious effects of oxygen upon this very porous material have not been presented.

The only known case of experimentation with the polymer base to produce a more radiation-hard fiber is shown in figures 9(a) and (b). These are blue-emitting fibers (425 nm) which display considerably greater resistance to attenuation changes as compared to the standard fiber of figure 5(a). In particular, the fiber of figure 9(b) is comparable in performance to the green (3HF) fiber of figure 5(b). Further experimentation with polymer bases is required before a proper evaluation of this approach can be made.

In conclusion, a great deal of accumulated experience has allowed the technology of producing polystyrene-based scintillators to be developed to a fine art, especially with regard to producing high quality scintillating optical fibers. Any new plastic bases will require a large body of careful development and evaluation before they can supplant polystyrene or polyvinyltoluene as the plastic base of choice for radiation-resistant scintillators.

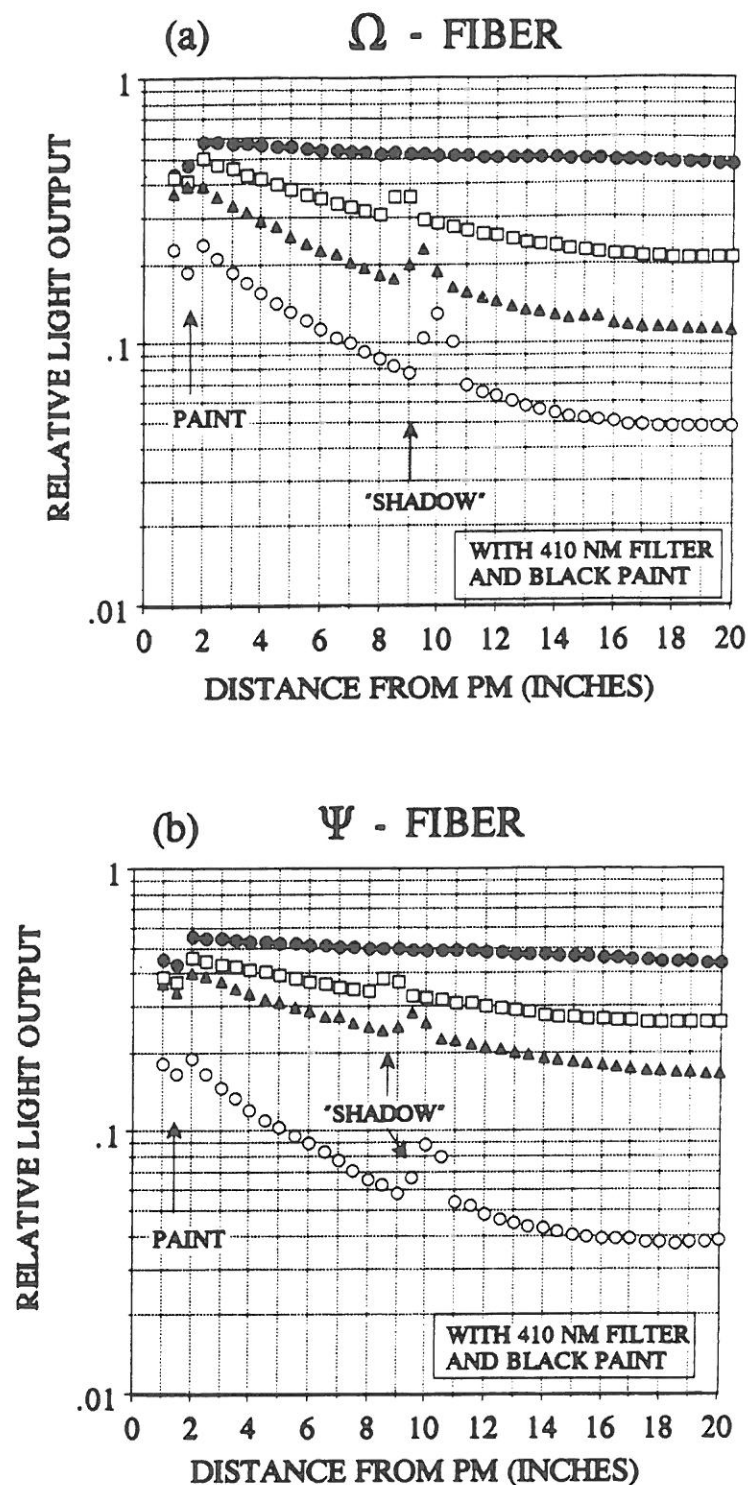


Figure 9: Attenuation curves for prototype radiation-hard *blue-emitting* (425 nm) fibers. These are the only known examples of scintillating fibers in which improvements in the radiation tolerance of the polymer base have been attempted. The legend of figure 5(a) applies here. One should compare the performance of these fibers with those shown in figure 5.

IV Where Do We Go From Here?

It is clear that although there has been considerable progress toward achieving a sufficiently radiation-hard scintillator, there are a number of key issues to be addressed before the subject can be closed.

The data seems to indicate that it will be necessary to check the effects of oxygen under low dose rate conditions. For polystyrene, it is likely than high dose rate tests can be safely extrapolated to realistic dose rate conditions when irradiations are done in air. Unfortunately, scintillating fibers use PMMA as a cladding, and this material has certainly shown sensitivity to oxygen at low dose rates. One can make the argument that optical damage to the micron-thick cladding will have no effect upon the performance of the fiber, but experimental verification is required.

In addition, the effect of irradiation upon fluors is insufficiently understood, particularly with regard to oxygen and concomitant dose rate effects. This is a subject currently under active investigation [3]. The results are eagerly awaited.

At present, the principle of waveshifting via large Stokes shift fluors has been the most successful method of improving the radiation resistance of scintillating fibers. Although some results with improved plastic bases seem promising, there are severe developmental hurdles to be overcome before they can be considered as serious alternatives to polystyrene. Research into better alternatives to 3HF are active, and one such possibility has been suggested at this workshop [16]. Also, a large Stokes shift, blue-emitting fluor, MOPOM, has been developed [17]. In liquid scintillation tests, this fluor was found to be extremely radiation-hard after a 10 Mrad exposure [18,19]. Plastic scintillators utilizing this dopant should be tested in the near future.

From previous arguments, it may be that a green-emitting scintillating fiber will be the preferred choice. If no good alternatives to 3HF are found, then it will be imperative that a systematic series of tests be performed in order to find the best 3HF fiber. Besides low dose rate experiments, a series of accelerated tests can be used to find some very useful information, namely, the role of concentration upon radiation resistance, both in terms of intrinsic scintillation losses and in terms of attenuation effects. This has an important bearing upon their use in detectors. Both tracking fibers and hadron calorimeters will require superb attenuation performance. Furthermore, some proposed tracking fibers have such thin diameters that only non-radiative transfer systems can be used, hence the need for an efficient, large Stokes shift fluor (perhaps MOPOM?). On the other hand, electromagnetic calorimeters will use short fibers, so that attenuation is not a critical issue. However the nature of the shower process will result in relatively localized damage in the module [20]. This implies that minimizing intrinsic scintillation losses will be of paramount importance. The PS/PTP/3HF system should provide an interesting test case for developing appropriate fibers for the different detectors (although a PS/MOPOM system may very well prove to be the superior choice for tracking fibers).

Finally, it will be imperative to test the interesting fibers in an appropriate detector mockup. There is already some initial testing of a low concentration 3HF fiber (and reported at this workshop [21]) for an electromagnetic calorimeter prototype. The early results indicate that significant performance changes can occur for sub-Mrad doses. It will be especially important to test annealing in such a mockup wherein the fibers are sealed

within another material.

V ACKNOWLEDGEMENTS

The author wishes to thank the representatives of Optectron, Kyowa and Bicron for their interest in this topic, and for the many samples that they generously donated. Additional thanks go to the organisers of the Tallahassee workshop for providing a forum of discussion for the problem of radiation resistance of plastic scintillators, as well as for providing the facilities of the FSU 3 MeV electron accelerator to irradiate the copious quantities of fiber samples. Finally, I thank S.M. and M.Z. for the many fruitful discussions on this topic.

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RADIATION EFFECTS ON SCINTILLATING FIBER OPTICS FOR SSC

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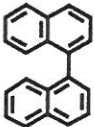
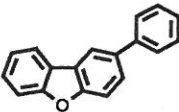
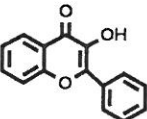
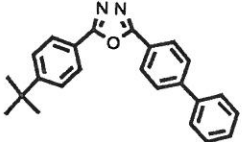
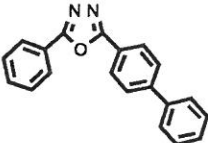
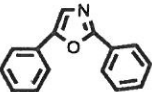
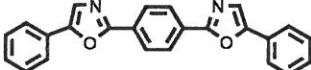
New polymer-based, dye-doped scintillators in the form of optical fibers are the basis of a new generation of particle detectors proposed for high-energy physics experiments. Radiation damage to the scintillation efficiency of these materials is a critical problem which must be surmounted to implement this technology. The major issues we are addressing are: identify radiation-induced color centers; determine kinetics of color center annealing; understand the role of oxygen in annealing (and formation?) of color centers; establish structure-property correlations for yield of color-center formation in different polymer types; evaluate potential stabilizer additives with respect to radiation-induced optical property changes; establish structure-property correlations for radiation-decomposition of different types of scintillator dyes; determine yields of colored radiolysis products of dyes; identify new strongly-red-shifted scintillator dyes to minimize the effects of color centers on light transmission; develop effective annealing schemes for removing color centers; develop and demonstrate predictive aging techniques for evaluating material lifetimes under low-level radiation conditions.

A study of the radiation degradation of 15 scintillator dyes has been completed. Recovery experiments following 100 Mrad γ -irradiation in toluene solution under inert atmosphere revealed a wide range in dye destruction yields (from ~0% loss to ~ 90% loss). The relative radiation stability of major scintillator types is: oligophenyls > oxazoles, oxadiazoles > polycyclic aromatics > stilbene. In polystyrene samples containing certain of these dyes (e.g., 3-HF, PPO), enhanced color center formation occurred (compared with pure polystyrene); other dyes (e.g., PTP, PDF, TS) did not significantly affect the radiation-discoloration of the polymer matrix. An extensive literature search identified several classes of organic dye molecules that are candidates for new red-shifted scintillators. These vary in their relative suitability in terms of their quantum yield, stokes shift, solubility, and expected radiation resistance. Synthesis of derivatives of certain of these dyes, which are projected to have superior optical properties, is in progress.

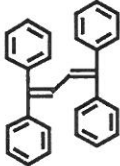
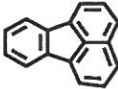
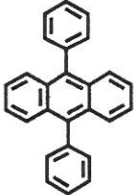
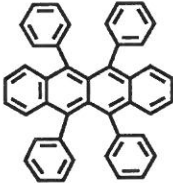
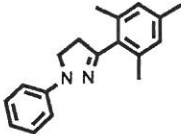
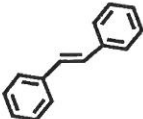
A survey of the radiation-induced absorbance of ~ 10 different types of optically-clear polymers has been completed. Different macromolecular types exhibited a wide variation in: 1) the extent of color center formation; 2) the rate of color center annealing (showing a strong correlation with oxygen permeation coefficient of the material); 3) the ratio of annealable and nonannealable color centers. Resistance to radiation-discoloration is poorly correlated with the relative resistance known for these polymers with respect to radiation-induced changes in mechanical properties. Poly- α -methyl styrene and an aliphatic, optical-grade, polyurethane were found to have relatively favorable radiation-optical properties. Several additives

of the hindered amine class show some promise as inhibitors of radiation-discoloration; hindered phenol stabilizer additives are found to result in increased discoloration. Thermal annealing experiments on γ -irradiated polystyrene are underway, in which color center disappearance rates are being measured at a series of temperatures. Arrhenius-type plots should yield activation energies for the annealing process, which will form the basis for predictive aging models. Experiments employing ESR spectroscopy, together with other analytical techniques, are underway to better identify the nature of radiation-induced color centers in polymers.

**Radiation Degradation Data for Scintillator Dyes γ -Irradiated
to 100 Mrad in Toluene Solution under Inert Atmosphere***

Name	Molecular Structure	Percent [†] Recovered
p-terphenyl		~ 100
DAT		90
binaphthyl		80
PDF		79
3HF		78
BPBD		67
PBD		48
PPO		62
POPOP		44

Radiation Degradation Data for Scintillator Dyes (cont.)

Name	Molecular Structure	Percent [†] Recovered
TPBD		58
Fluoranthene		56
DPA		49
Rubrene		26
PMP		35
trans-stilbene		16

* Analysis of samples was performed using Gas chromatography, with the exception of rubrene and POPOP, which were analyzed using liquid chromatography. Initial concentration of dyes was 10 mg/ml, except for POPOP, which was irradiated at 6 mg/ml.

† Experimental scatter in the data averaged $\pm 10\%$.

STABILIZERS BEING EVALUATED FOR SUPPRESSION OF COLOR CENTER FORMATION
IN γ -IRRADIATED POLYSTYRENE

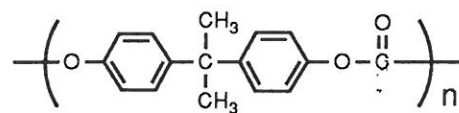
The first three are hindered amines; the last is a hindered phenol

<u>Stabilizer</u>	<u>Structure</u>
Tinuvin 770	
Tinuvin 622	
Goodrite UV-3034	
Antioxidant 2246	

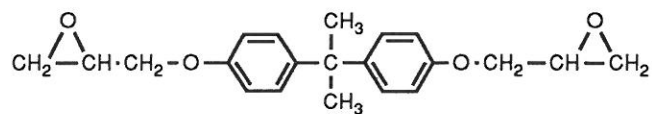
Polymer	Structure
Poly(4-methyl pentene)	$\left(\text{CH}_2 - \underset{\substack{ \\ \text{CH}_2 \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_3}}{\text{CH}} \right)_n$
Polysulfone	$\left(\text{C}_6\text{H}_4 - \underset{\substack{ \\ \text{CH}_3 \\ \\ \text{CH}_3}}{\text{C}} - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - \text{SO}_2 - \text{C}_6\text{H}_4 - \text{O} \right)_n$
Poly(1,4-phenylene ether sulfone)	$\left(\text{C}_6\text{H}_4 - \text{SO}_2 - \text{C}_6\text{H}_4 - \text{O} \right)_n$
Poly(α-methyl styrene)	$\left(\text{CH}_2 - \underset{\substack{ \\ \text{C}_6\text{H}_5}}{\overset{\text{CH}_3}{\text{C}}} \right)_n$
Polystyrene	$\left(\text{CH}_2 - \underset{\substack{ \\ \text{C}_6\text{H}_5}}{\text{CH}} \right)_n$
Polymethylmethacrylate	$\left(\text{CH}_2 - \underset{\substack{ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{CH}_3}}{\overset{\text{CH}_3}{\text{C}}} \right)_n$
Polyvinyl chloride	$\left(\text{CH}_2 - \underset{\substack{ \\ \text{Cl}}}{\text{CH}} \right)_n$
Polyurethane	$\left(\text{O} - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{O} - \text{C}(=\text{O}) - \text{NH} - \text{C}_6\text{H}_{10} - \text{CH}_2 - \text{C}_6\text{H}_{10} - \text{NH} - \text{C}(=\text{O}) - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{O} \right)_n$ <p align="center">(highly cross-linked)</p>

Polymer**Structure**

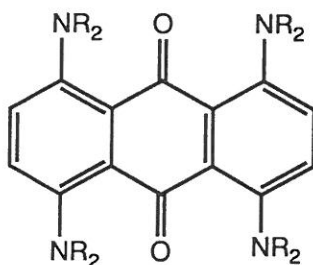
Polycarbonate



Epoxy



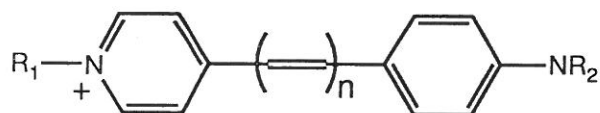
(cross-linked with
diethanolamine)



Anthraquinone Dyes

$$\Phi_f < 0.1$$

$$\lambda_{\max}(\text{fl}) = 730\text{-}815 \text{ nm}$$



Pyridinium Dyes

$$\lambda_{\max}(\text{fluor}) \approx 600 \text{ nm } (n=2),$$

$$\approx 700 \text{ nm } (n=3),$$

for $R=\text{Me}$, $R_1=\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$:

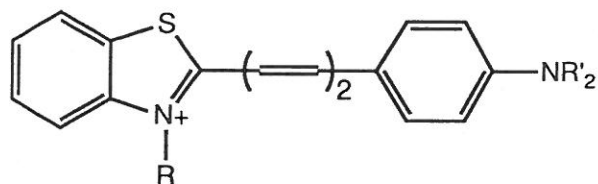
Φ_f = solvent dependent (x100)

$$\lambda_{\max}(\text{abs}) = 500 \text{ nm}$$

$$\lambda_{\max}(\text{fl}) = 610 \text{ nm}$$

Radiation Stability Problematic?

Ionic



Styryl Dyes

$$\lambda_{\max}(\text{fl}) \approx 700 \text{ nm},$$

for $R=\text{C}_2\text{H}_5$, $R'=\text{CH}_3$:

$$\Phi_f = 0.7$$

$$\lambda_{\max}(\text{abs}) = 560 \text{ nm}$$

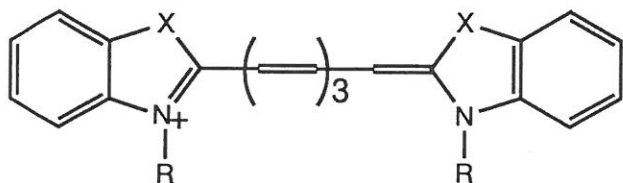
$$\lambda_{\max}(\text{fl}) = 704 \text{ nm},$$

Highly self-absorbed

Radiation Stability Problematic?

Ionic

X = O, S, C(Me₂)



Tricarbo-cyanine Dyes

$\lambda_{\max}(\text{fl}) \approx 700 \text{ to } >900 \text{ nm}$,

for R = C₂H₅, X = O, n = 3:

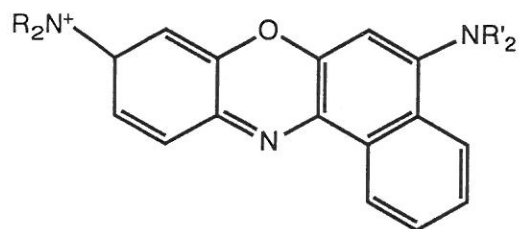
$\Phi_f = 0.49$

$\lambda_{\max}(\text{abs}) = 695 \text{ nm}$

$\lambda_{\max}(\text{fl}) = 719 \text{ nm}$

Radiation Stability Problematic?

Ionic

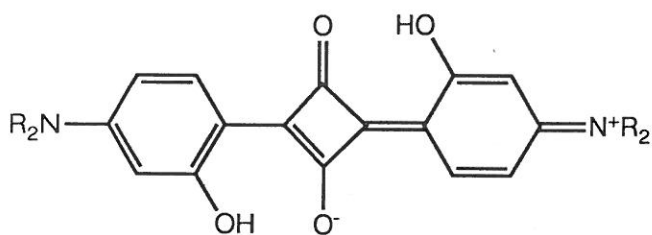


Oxazine Dyes

$\lambda_{\max}(\text{fl}) \approx 600\text{-}700 \text{ nm}$

for R' = H:

	R = C ₂ H ₅	R = H
Φ_f	0.23	0.59
$\lambda_{\max}(\text{abs})$	627 nm	593 nm
$\lambda_{\max}(\text{fl})$	660 nm	615 nm
Ionic		



Squarylium Dyes

$\lambda_{\max}(\text{fl}) \approx 640\text{-}680 \text{ nm}$

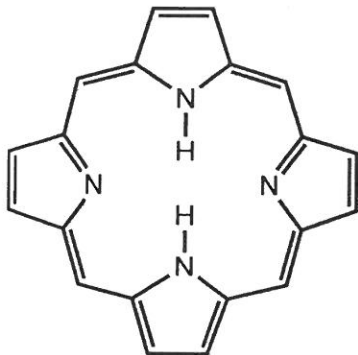
for R = C₂H₅:

$\Phi_f = 0.86$

$\lambda_{\max}(\text{abs}) = 641 \text{ nm}$

$\lambda_{\max}(\text{fl}) = 662 \text{ nm}$

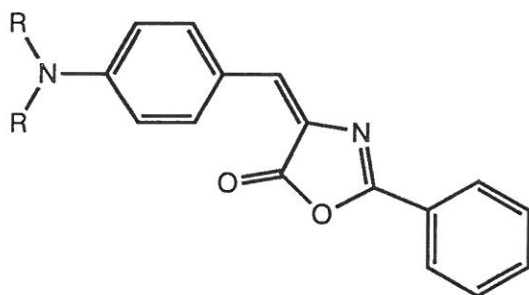
Radiation Stability Problematic?



Porphyrin Dyes

$\Phi_f < 0.1$

$\lambda_{\max}(\text{fl}) = 650\text{-}710 \text{ nm}$



Oxazolone Dyes

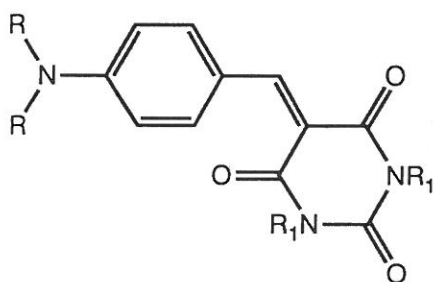
for $R = \text{CH}_3$:

$\Phi_f (\text{soln}) \approx 0$

$\lambda_{\text{max}}(\text{abs, soln}) = 470 \text{ nm}$

$\lambda_{\text{max}}(\text{fl, crystal}) = 640 \text{ nm}$

$\lambda_{\text{max}}(\text{fl, PS matrix}) = 528 \text{ nm}$



Barbituric Acid Dyes

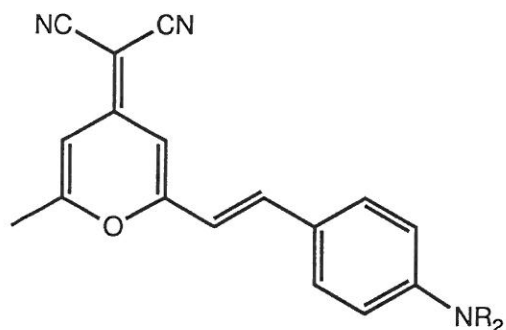
for $R = \text{CH}_3$, $R_1 = \text{H}$ or CH_3 :

$\Phi_f (\text{soln}) \approx 0$

$\lambda_{\text{max}}(\text{abs, soln}) = 467 \text{ nm}$

$\lambda_{\text{max}}(\text{fl, crystal}) = 610 \text{ nm}$

$\lambda_{\text{max}}(\text{fl, PS matrix}) = 522 \text{ nm}$



Merocyanine Dyes

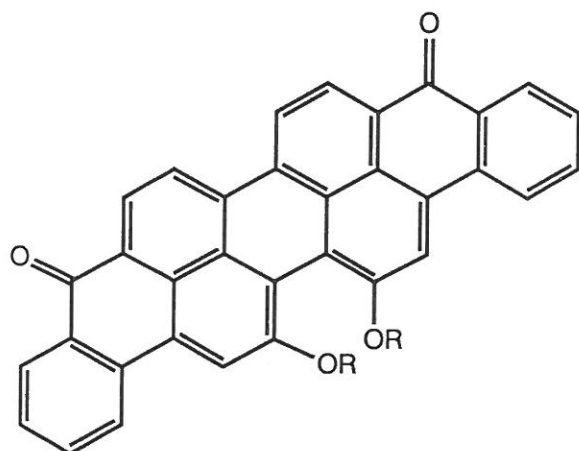
for $R = \text{CH}_3$, "DCM"

$\Phi_f = 0.71$

$\lambda_{\text{max}}(\text{abs}) = 480 \text{ nm}$

$\lambda_{\text{max}}(\text{fl}) = 627 \text{ nm}$ (polar solvents)

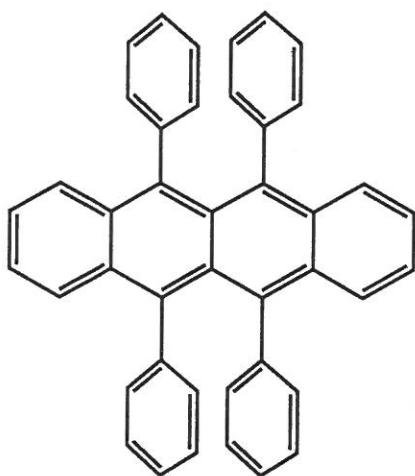
Radiation Stability Problematic?



Violanthrone Derivatives

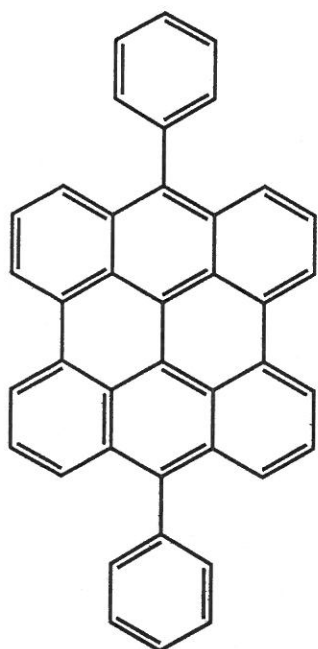
	R=Me	R=COCH ₃
Φ_f	0.29	0.67
$\lambda_{\max}(\text{abs})$	658 nm	582 nm
$\lambda_{\max}(\text{fl})$	720 nm	625 nm

Absorption tail to 1 μm



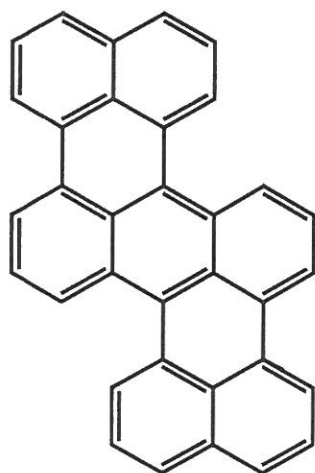
Rubrene

$\Phi_f = 0.98$
$\lambda_{\max}(\text{abs}) = 530 \text{ nm}$
$\lambda_{\max}(\text{fl}) = 560 \text{ nm}$



4,11-Diphenylbisanthene

$\Phi_f = 0.10$
$\lambda_{\max}(\text{abs}) = 694 \text{ nm}$
$\lambda_{\max}(\text{fl}) = 730 \text{ nm}$

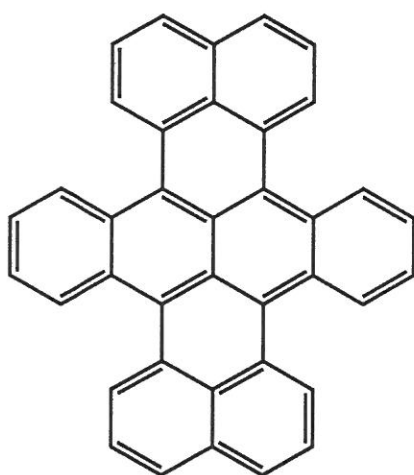


Tetrabenzopentacene

$$\Phi_f = 0.51$$

$$\lambda_{\max}(\text{abs}) = 628 \text{ nm}$$

$$\lambda_{\max}(\text{fl}) = 690 \text{ nm}$$

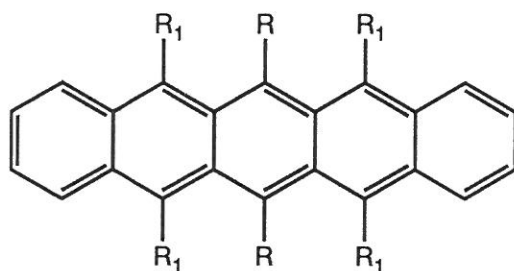


Dibenzoterrylene

$$\Phi_f = 0.21$$

$$\lambda_{\max}(\text{abs}) = 750 \text{ nm}$$

$$\lambda_{\max}(\text{fl}) = 630, 810 \text{ nm}$$



Pentacene Derivatives

$R=H$, $R_1=\text{Phenylethynyl}$

$$\Phi_f = 0.08$$

$$\lambda_{\max}(\text{abs}) = 705 \text{ nm}$$

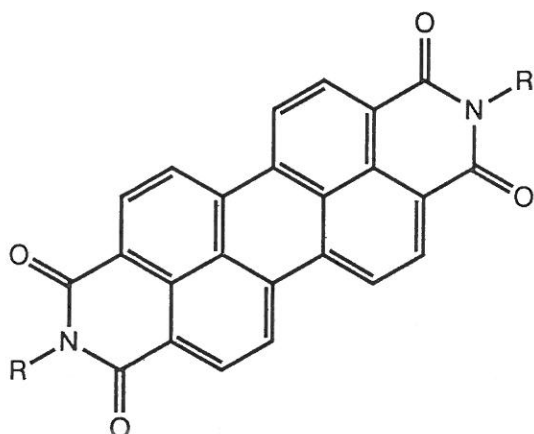
$$\lambda_{\max}(\text{fl}) = 740 \text{ nm}$$

$R=\text{Phenylethynyl}$, $R_1=H$

$$\Phi_f = 0.26$$

$$\lambda_{\max}(\text{abs}) = 668 \text{ nm}$$

$$\lambda_{\max}(\text{fl}) = 680 \text{ nm}$$



Perylenetetracarboxylic acid Diimides, $R=\text{alkyl, aryl}$;

for $R = \text{phenyl}$:

$$\Phi_f = 0.93$$

$$\lambda_{\max}(\text{abs}) = 515 \text{ nm}$$

$$\lambda_{\max}(\text{fl}) = 530 \text{ nm}$$

Contribution to the Workshop on Radiation Hardness of Plastic Scintillator

PROGRESS ON DESIGN OF RADIATION-HARD SCINTILLATORS

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Abstract

New fluors from the oligophenylene family, especially terphenyls with *tertiary* alkyl auxofluors and certain sexiphenyls and quaterphenyls containing a 9,9-dialkylfluorene structure, were found to have excellent radiation hardness, high light output, excellent resistance to oxygen and to chemical quenching, and short fluorescence decay times. Their self-absorption would appear to limit their use to bulk scintillators. New pyrazolines related to PMP were prepared to circumvent yellowing by oxygen with some success; but recent findings that this class of fluor has poor radiation hardness and slow decay times mitigate against the use of pyrazolines in general. The structural feature of the PMP molecule that confers its large Stokes' shift, which is the single most desirable property of PMP, was found to be applicable to the POPOP molecule. The derivative called MOPOM, which has a larger Stokes' shift than POPOP, was also found to give, when dissolved in 1-phenylnaphthalene, good radiation hardness, high light output, short decay time, and low oxygen sensitivity.

Introduction

The general properties of organic scintillators have been reviewed recently (Flournoy,88). The special requirements of fluors for scintillating fibers, especially for use with the superconducting super-collider, are: (1) radiation-hardness to 10^{4-6} Gy (Clough, this Proc.); (2) emission at wavelengths >400 nm; (3) very low absorption at these wavelengths (Destruel,89); (4) light output $>10\%$ of that of standard plastic scintillators; and (5) sufficient solubility in an aromatic solvent or monomer.

We reported excellent radiation-hardness for a number of oligophenylenes originally designed as laser dyes (Kauffman,87; 88a; 88b). New compounds from this series were prepared to obtain better solubility and radiation-hardness. These results are described below.

The pyrazoline known as PMP was reported to have the best overall properties of a variety of fluors tested in poly(methylphenylsiloxane) (PMPS) in an argon atmosphere (Bowen,88b). PMP had very high light output at very high concentrations in 1-methyl- and 1-phenylnaphthalene solution which could be used in capillary light guides (Ruchti,88). We studied derivatives of PMP in order to obtain one resistant to decomposition by oxygen, and to obtain a green-emitting wavelength wavelength shifter from this class.

The structural feature of PMP which provides its large Stokes' shift had not been

applied to the classic fluor POPOP. Since the more soluble Dimethyl-POPOP is still widely used in polystyrene because low concentrations provide high light output (Bross,88), we prepared new derivatives of POPOP with greater Stokes' shift.

Finally, the importance to both high light output and short fluorescence decay time of high extinction coefficient (ϵ) is emphasized.

New Oligophenylenes

Recent development of bridged oligophenylenes as fluors (Kauffman,88b) compared the 3 quaterphenyls and 1 sexiphenyl in Fig. 1. The names "OLIGO 374A", etc., are derived from the fluorescence or lasing peak wavelength of each compound. The siloxane polymer (Fig. 2) is much more radiation resistant than poly(vinyltoluene), (PVT), the matrix of BC 408. Note that the initial light output of PMP at 9x the concentration of OLIGO 374A was less than twice as great, and that all of the oligophenylenes were more radiation-hard in air than PMP. Within the group of quaterphenyls, the presence of oxygen in the side-chains (OLIGO 373) or on the ends of the long axis of the fluorophor as auxofluors (OLIGO 395) was detrimental. Despite its plethora of oxygens, OLIGO 415 was more radiation-hard than OLIGO 374A, an oxygen-free hydrocarbon. This follows the order of the unsubstituted oligophenylenes: the more rings, the more stable (Bowen,88a). Bowen has observed that the removal of all oxygens from OLIGO 415 should give an extremely radiation-hard fluor. We prepared such a sexiphenyl, called OLIGO 408, and can report, qualitatively, that when it was incorporated into PMPS with a new primary fluor described below, high light output with very good radiation-hardness was observed (S. Majewski thru C. R. Hurlbut, priv. commun.,90). Other properties of OLIGO 408 are described below.

The last entry under Fluors in Fig. 2 is OLIGO 415 plus DMT. DMT, whose structure is shown in Fig. 3, is not radiation-hard when tested alone, has a low fluorescence quantum yield (Φ), and its fluorescence peak is at too short a wavelength for good matching with the absorption of OLIGO 415 (Zapka,79). It was used simply because it was the only p-terphenyl derivative available with enough solubility in PMPS, which is a much poorer solvent than PVT.

We prepared 4,4"-di-t-amylterphenyl OLIGO 351), which is very soluble in PVT, but not quite soluble enough in PMPS (Kauffman,88b). With its high ϵ of 38,000 vs. only 30,000 for terphenyl, OLIGO 351 proved an outstanding primary fluor for liquid scintillation counting, as described below. The subtle change of substituent from t-amyl (dimethylethyl) to 3-methyl-3-pentyl (diethylmethyl) was carried out, and the new terphenyl was soluble enough in PMPS with no loss of other desirable properties (Fig. 3).

When the performance of OLIGO 351 and OLIGO 408 in polymer was beginning to be recognized, we thought it would be of interest to compare them with classical fluors for light output and resistance to chemical quenching in some liquid systems. A preliminary report was made (Wunderly,90a) and a detailed paper which lists several of the new fluors under different names is in press (Wunderly,90b).

The structural formulas of the most common classical fluors are given: primary in Fig. 4 and one primary and wavelength shifters in Fig. 5. TP was the first primary fluor in common use, is still the most common in plastic scintillators today; but was supplanted by PPO in liquids because of the far higher solubility and compatibility with

water of PPO in early liquid scintillation (LS) cocktails. PPO also had better spectral matching with the early photomultiplier (PM) tubes, and worked well with the wavelength shifter POPOP. PBD had much better resistance to chemical quenching than PPO. The more soluble Butyl-PBD became the primary fluor of choice for chemically-quenched samples, and remains so.

BIBUQ (Fig. 5), a primary with emission at 386nm, and not enhanced by the common wavelength shifters, was found to have very high light output at high concentration, due to the presence of solubilizing groups that make up 2/3 of the mass of the molecule. Like other unbridged oligophenylenes, BIBUQ is very susceptible to chemical quenching, and never found wide use. The early wavelength shifter POPOP and its more soluble derivative Dimethyl-POPOP are used at present; but the more soluble and acid-resistant Bis-MSB is the wavelength shifter of choice today in *liquid* systems for *beta* counting.

The structures of our new oligophenylene fluors are shown in Figs. 5 and 6. These include 3 bridged quaterphenyls of which one is OLIGO 374A, reported above as effective in PMPS; one bearing methoxy groups as auxofluors (OLIGO 386A), and one bearing t-amyl auxofluors (OLIGO 380B). The new bridged sexiphenyl optimized as a fluor (OLIGO 408) and di-t-amylterphenyl (OLIGO 351) are shown.

The relative photon outputs of various fluor combinations in pseudocumene are shown in Fig. 8. Experimental details have been given (Wunderly,90b). All of the bridged oligophenylenes, without wavelength shifter, had higher light output than the classic fluors with or without wavelength shifter. DitAmTP (OLIGO 351) had higher photon output than PPO despite its disadvantage in wavelength (351 nm vs. 365 nm).

When the chemical quencher nitromethane was added to the above samples (Fig. 9), the relative effectiveness of the fluors changed radically. DitAmTP was quenched in the manner of BIBUQ. The 3 bridged quaterphenyls were superior to PPO with or without wavelength shifter. Butyl-PBD was significantly better than all of these. However, OLIGO 408 established a new standard of quench resistance.

Because of its expense at present, we tested OLIGO 408 as a wavelength shifter in pseudocumene (Fig. 10). It was superior to Bis-MSB with both PPO and Butyl-PBD; but gave the highest photon output with DitAmTP, even higher than its output as a primary. This combination should find application in bulk scintillators which are not quenched, where high light output and excellent radiation-hardness are desired. The Stokes' shift is too small for use in fibers.

When these samples were quenched with nitromethane (Fig. 11) the best combination with OLIGO 408 as a wavelength shifter contained Butyl-PBD as a primary. This combination should find application in metal-loaded or otherwise quenched bulk scintillators, where high light output and excellent radiation-hardness are desired.

Pyrazolines Related to PMP

The pyrazoline PMP (Cpd. 3 in Fig. 12) has several desirable properties as a fluor for scintillating fibers (Destruel,89), among which are (1) high Φ , (2) high solubility, and (3) a very large Stokes' shift (Güsten,78), caused by a large change in conformation between the ground state, in which the two benzene rings are at $\approx 90^\circ$ angles with the pyrazoline ring (Fig. 12A), and the planar S1 state. It was thought to

have good radiation-hardness, at least in PMPS under argon (Bowen,88a,88b,89), but not when exposed to air. We began a program to address this oxygen reactivity, which leads to aromatization of the pyrazoline ring, by synthesis of certain derivatives (Fig. 12). The actual syntheses will be described elsewhere.

Compounds 1 and 2 had been prepared; we repeated the synthesis to determine photophysical properties. The hydrogen atoms on C5 of the pyrazoline ring were substituted by methyl groups. This led to a 5% drop in ϵ , no significant change in Φ , no change in the wavelength of emission, and a significant hypsochromic shift in absorption (increasing the Stokes' shift). A simple experiment was carried out by bubbling oxygen thru chloroform solutions of these compounds, in which 2 was ≈ 10 times as resistant to yellowing as 1. These compounds and PMP were tested for radiation-hardness in PVT. None were acceptably radiation-hard (C. R. Hurlbut, priv. commun.,89).

Because the usual depiction of electron-flow for excitation of 2-pyrazolines (Fig. 14) indicated that an electron-releasing group on N1 might enhance this transition, we made the t-butyl derivative 4. This displayed a very low value of Φ , indicating that some other mode of electron movement may be more important to formation of the S1 state.

In an effort to obtain an extreme Stokes' shift, a pyrazoline with both a 3-mesityl and 5,5-dimethyl groups (5) was synthesized. While we are still attempting to purify it, we can say that its Φ is low, and at the absorption peak we believe represents the 0-0 transition, ϵ is very low.

Before we were aware of the lack of radiation-hardness of PMP (Puseljc,90), we attempted to prepare a green-emitting dipyrazoline for use in fibers. The idea was to skirt the radiation-damage-induced absorption of PVT in the 400-500 nm range (Bowen,88a). Considerable work had been reported (Leggate,68) on attempts to prepare derivatives of dioxazoles, dioxadiazoles, and dipyrazolines with bathochromic shifts of emission from the parent compounds. In molecules with equal numbers of aromatic rings, dipyrazolines showed emission at the longest wavelengths. Oddly, in all 3 series of compounds, increasing the length of the oligophenylene bridge between the heterocyclic rings did not give the expected bathochromic shifts (Fig. 13). This was explained by saying that the "normal" (but discredited by our observations on 5 in Fig. 12) electron flow led to isolated smaller chromophores (Fig. 14). We thought that the well-known ability of the 5-membered ring in fluorene to stabilize a negative charge would at least give a dipyrazoline with a very high ϵ . Thus we prepared the dipyrazoline in Fig. 15 with its fluorene center. The longest wave absorption band had abnormally low ϵ — so low as to indicate that the electron flow to form the S1 state is probably opposite to what is normally depicted! This supports the inference one may draw from the low value of Φ we found for 5 in Fig. 12.

Because of the lack of radiation-hardness of PMP in either 1-phenylnaphthalene or in PVT reported recently, as well as its oxygen sensitivity, we plan no further work with pyrazolines. However, the effect of the mesityl group in PMP (see Fig. 12) on its Stokes' shift seemed likely to apply to compounds that are better fluors to begin with, such as POPOP.

Derivatives of POPOP with Greater Stokes' Shift

The Los Alamos group responsible for so much early fluor development found that 2-(2-fluorenyl)oxazole (Fig. 16) which bears a 5-mesityl group had a much greater Stokes' shift than the corresponding 5-phenyl compound. Moreover, there was no drop in ϵ .

Therefore, we decided to make the dimesityl derivative of POPOP called "MOPOM", and also an analog where the terminal auxofluors were t-butyl rather than methyl called "DBTeM-POPOP" because of the superior performance of di-t-amylterphenyl reported above. An increase in Stokes' shift from 53 nm to 82 nm was achieved (Fig. 17) with no drop in ϵ from POPOP to MOPOM, and a 6% drop for DBTeM-POPOP. (Note that substitution of mesityl for phenyl in PMP gave a 30% drop in ϵ .)

Saturated solutions of MOPOM and DBTeM-POPOP in 1-phenylnaphthalene had a relative photon output equal to that of BC-501 plastic scintillator (Kennedy,90). Used as primary fluors they can provide a means of reaching much longer wavelengths efficiently when wavelength shifters with appropriate spectral properties are made available. The fluorescence decay time of MOPOM was ≈ 2 nsec, and of DBTeM-POPOP ≈ 2.5 nsec. These were faster times than those of a number of other high Stokes' shift fluors tested (Puseljic,90). MOPOM and DBTeM-POPOP were radiation-hard to 10^5 Gy; both are significantly harder than PMP. DBTeM-POPOP has no advantage over MOPOM. Further variations on MOPOM are planned. Presently MOPOM appears to be among the best fluors for scintillating fibers, and may serve until improved proton-transfer fluors are developed (Kasha, this Proc.).

Importance of High Extinction Coefficient

The relation of emission intensity or photon output to ϵ is shown in Fig. 18. Where FQE (which = Φ) is the same, light output is proportional to ϵ . Thus a fluor such as MOPOM ($\epsilon = 48,000$) may equal the light output of PMP ($\epsilon = 16,000$) at 1/3 its concentration. Lower concentration allows a smaller Stokes' shift. With $\epsilon = 86,000$, OLIGO 408 and OLIGO 415 ($\epsilon = 90,000$) are in a class by themselves, hampered only by a small Stokes' shift in providing high light output in fibers.

Short fluorescence decay time is desirable for counting at high flux rates and distinguishing particles with similar "arrival" times. The inverse relationship between fluorescence decay time and ϵ is well established (Berlman,68), at least in oligophenylene-like molecules. OLIGO 408 was found to have a fluorescence decay time of 1.1 nsec (Flournoy, priv. commun.,89; experimental details in Fluornoy,88); MOPOM 2 nsec, and PMP 6 nsec (Puseljic,90).

High ϵ is also a property of laser dyes with high energy output, and seems to be associated with symmetry of the fluorophor. Oligophenylenes with symmetrical auxofluors have more energy output than those without (Kauffman,90). The new pyrromethene-BF₂ dyes (Boyer,90; Davenport,90) and all rhodamines have this element of symmetry, while coumarins, PMP, some oxazoles and most proton-transfer dyes do not.

Supplemental Material

A package of 25 absorption and fluorescence spectra of compounds mentioned in this paper will be sent to anyone who provides a self-addressed 9x12 inch envelope.

Acknowledgments

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Fig.1. Structures of New Bridged Oligophenylenes

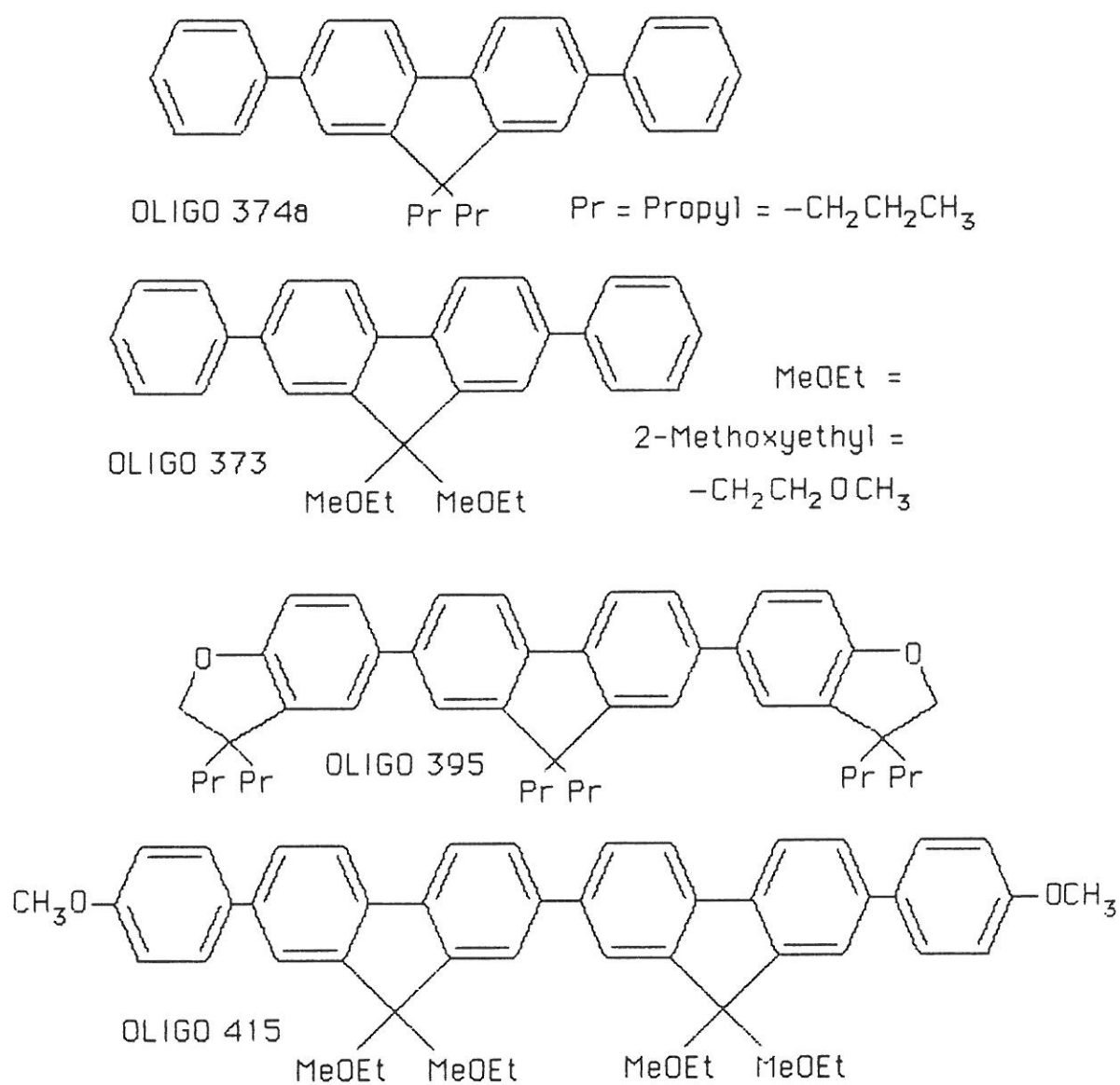
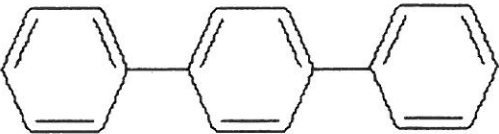
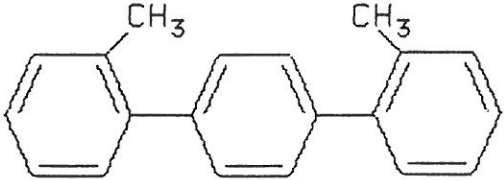
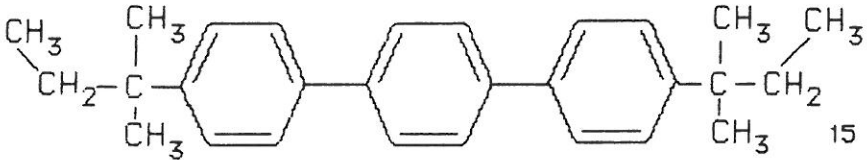
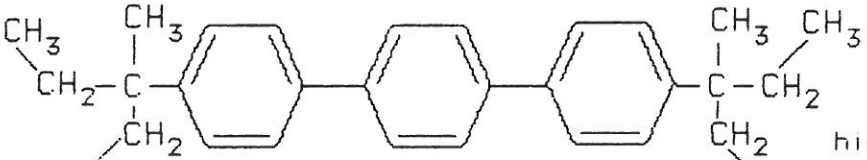


Fig. 2. Radiation-Hardness and Related Scintillation Properties of New Bridged Oligophenylene Fluors in Poly(methylphenylsiloxane) (Bowen, 88a,b).

Fluor(s)	Conc.(w/w)	Lifetime*	Peak Emission	Relative Initial Light Output**
BC408 Reference Standard	--	2 MRad	≈410nm	100
PMP	1.8%	3	425	90
OLIGO 395	0.2	5	400	25
OLIGO 373	0.1	5.5	375	35
OLIGO 374a	0.2	13	375	55
OLIGO 415	0.02	18.5	415	5
OLIGO 415 + DMT	0.01 0.35	18.5?	415	45

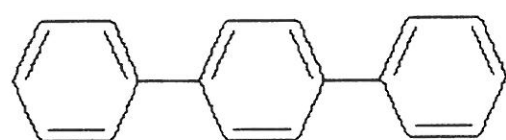
*Radiation dose to sample in air from cobalt-60 that caused 50% drop in light output **Corrected for response of phototube detector (Hamamatsu Type R1477)

Figure 3. Structure-Stability Correlations for Some p-Terphenyls

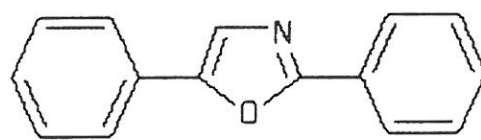
Structure and Name of Laser Dye or Fluor	Lifetime as Fluor*	Comments
 <p>terphenyl</p>	≈ 10 MRad	Rad-Hard Good Light Output Insoluble
 <p>2,2''-dimethylterphenyl (DMT)</p>	6	Rad-Soft Fair Light Output Soluble
 <p>4,4''-di-t-amylterphenyl (OLIGO 351)</p>	15	Rad-Hard Good Light Output Soluble in PVT; not in PMPS
 <p>4,4''-(3-methyl-3-pentyl)terphenyl</p>	high**	Rad-Hard Good Light Output Soluble in PVT and in PMPS

*Energy absorbed from cobalt-60 (1.3 & 1.7 MeV) by fluor at optimum concentration in PMPS until pulse height falls by 50% (Zorn, 88); value for terphenyl guesstimated from data in PVT; is to be redetermined in PMPS. **Majewski thru Hurlbut, 1990.

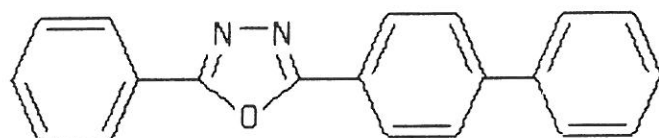
Fig.4. Structures of Classical Fluors used in Liquid Scintillation Counting



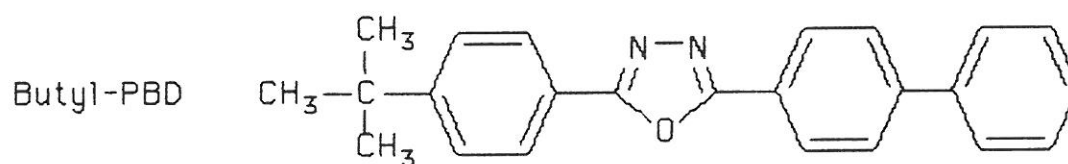
TP p-terphenyl



PPO 2,5-diphenyloxazole

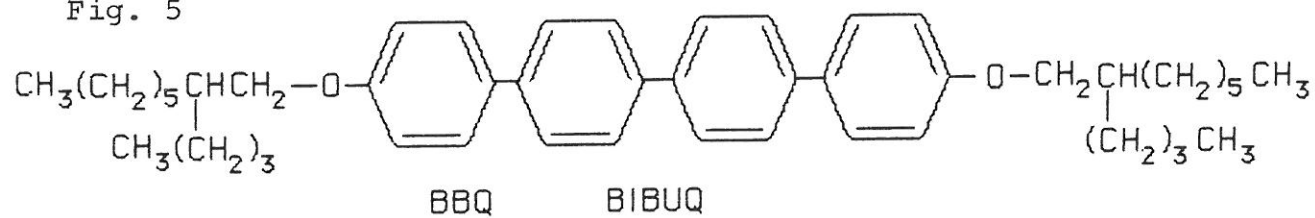


PBD



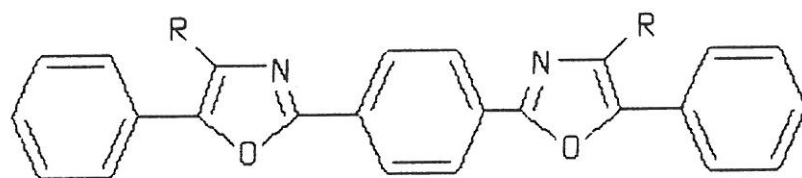
Butyl-PBD

Fig. 5

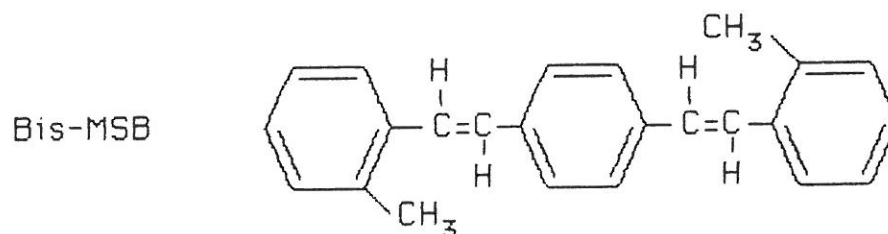


BBQ

BIBUQ



R=H: POPOP

R=CH₃: Dimethyl-POPOP
DM-POPOP

Bis-MSB

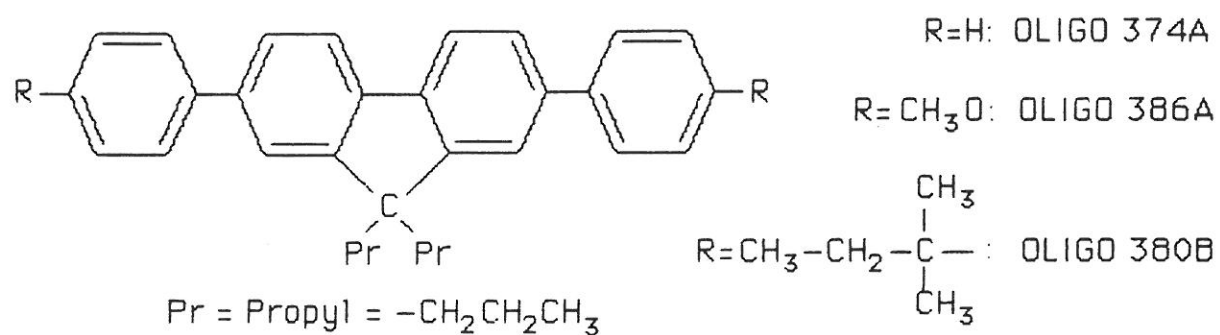


Fig.6.Structures of New Oligophenylene Fluors

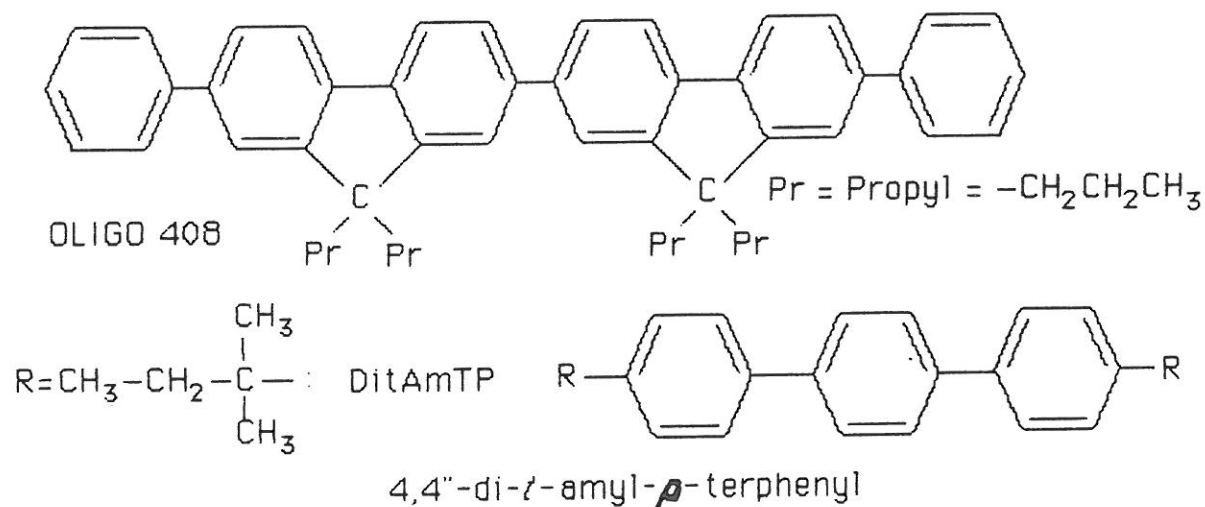


Fig.7.Structures of New Oligophenylene Fluors

Fig.8. Relative Photon Output (RPO) of New Oligophenylenes
as Primary Fluors in Air-Quenched Cocktail in Pseudocumene

Primary Fluor 2.26x10 ⁻² M	Shifter 1.61x10 ⁻⁵ M	H-Number on Beckman 3801	RPO
OLIGO 408	—	1.5	106.6
OLIGO 374A	—	4.5	103.9
OLIGO 374A	Bis-MSB	7.0	101.7
OLIGO 386A	—	8.0	100.9
OLIGO 380B	—	8.0	100.9
Butyl-PBD	Bis-MSB	9.5	100.0
Butyl-PBD	—	11.5	97.9
PPO	Bis-MSB	18.8	91.9
DitAmTP	—	20.0	90.9
PPO	—	30.0	83.4

Fig.9. Relative Photon Output (RPO) of New Oligophenylenes
as Primary Fluors in Nitromethane-Quenched Cocktail

Primary Fluor 2.26x10 ⁻² M	Shifter 1.61x10 ⁻⁵ M	H-Number on Beckman 3801	RPO
OLIGO 408	—	124	128.4
Butyl-PBD	Bis-MSB	150	100.0
Butyl-PBD	—	152	98.4
OLIGO 386A	—	176	77.7
OLIGO 374A	Bis-MSB	188	69.0
PPO	Bis-MSB	199	61.4
OLIGO 374A	—	208	56.0
OLIGO 380B	—	212	53.7
PPO	—	220	49.1
DitAmTP	—	222	48.0

Fig. 10. Relative Photon Output (RPO) of Primary Fluors
in Air-Quenched Cocktail using OLIGO 408 as Shifter in Pseudocumene

Primary Fluor 2.26x10 ⁻² M	Shifter	H-Number on Beckman 3801	RPO
DitAmTP	OLIGO 408*	0.5	107.5
OLIGO 408	—	1.5	106.6
Butyl-PBD	OLIGO 408*	1.8	106.4
Butyl-PBD	Bis-MSB**	9.5	100.0
PPO	OLIGO 408*	13.5	96.2
PPO	Bis-MSB**	18.8	86.2
*1.61x10 ⁻⁵ M **7.7x10 ⁻⁶ M			

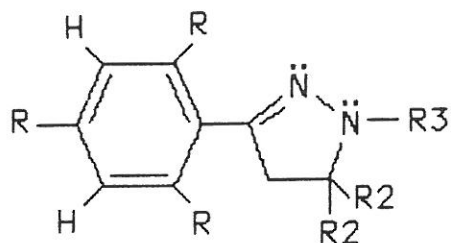
Fig. 11. Relative Photon Output (RPO) of Primary Fluors
in Nitromethane-Quenched Cocktail using OLIGO 408 as Shifter in Pseudocumene

Primary Fluor 2.26x10 ⁻² M	Shifter	H-Number on Beckman 3801	RPO
OLIGO 408	—	124	128.4
Butyl-PBD	OLIGO 408*	130	121.6
Butyl-PBD	Bis-MSB**	150	100.0
DitAmTP	OLIGO 408*	175	78.8
PPO	OLIGO 408*	187	70.0
PPO	Bis-MSB**	199	61.4
*1.61x10 ⁻⁵ M **7.7x10 ⁻⁶ M			

Fig. 12.
PHOTOPHYSICAL PROPERTIES
OF PYRAZOLINES RELATED TO
PMP

*this work

**Destruel, 89



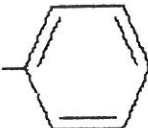
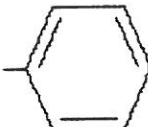
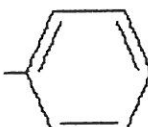

Cpd.	R	R2	R3	Abs	Fl Em	FQE
1	H	H		355nm($\epsilon=20,000$)	427nm	67%
2*	H	CH ₃		343 (19,000)	428	68
3** PMP	CH ₃	H		290 (14,000)	425	88
4*	H	H	-C(CH ₃) ₃	-	-	low
5*	CH ₃	CH ₃		could not purify	-	low

Fig. 12A. Lowest-energy conformation of PMP in the ground state, showing 86° and 89° angles between the benzene rings and the pyrazoline ring. Calculated by v.5.10 of MOPAC MNDO or PM3 using the CAChe Worksystem of Tektronix by David Gallagher.

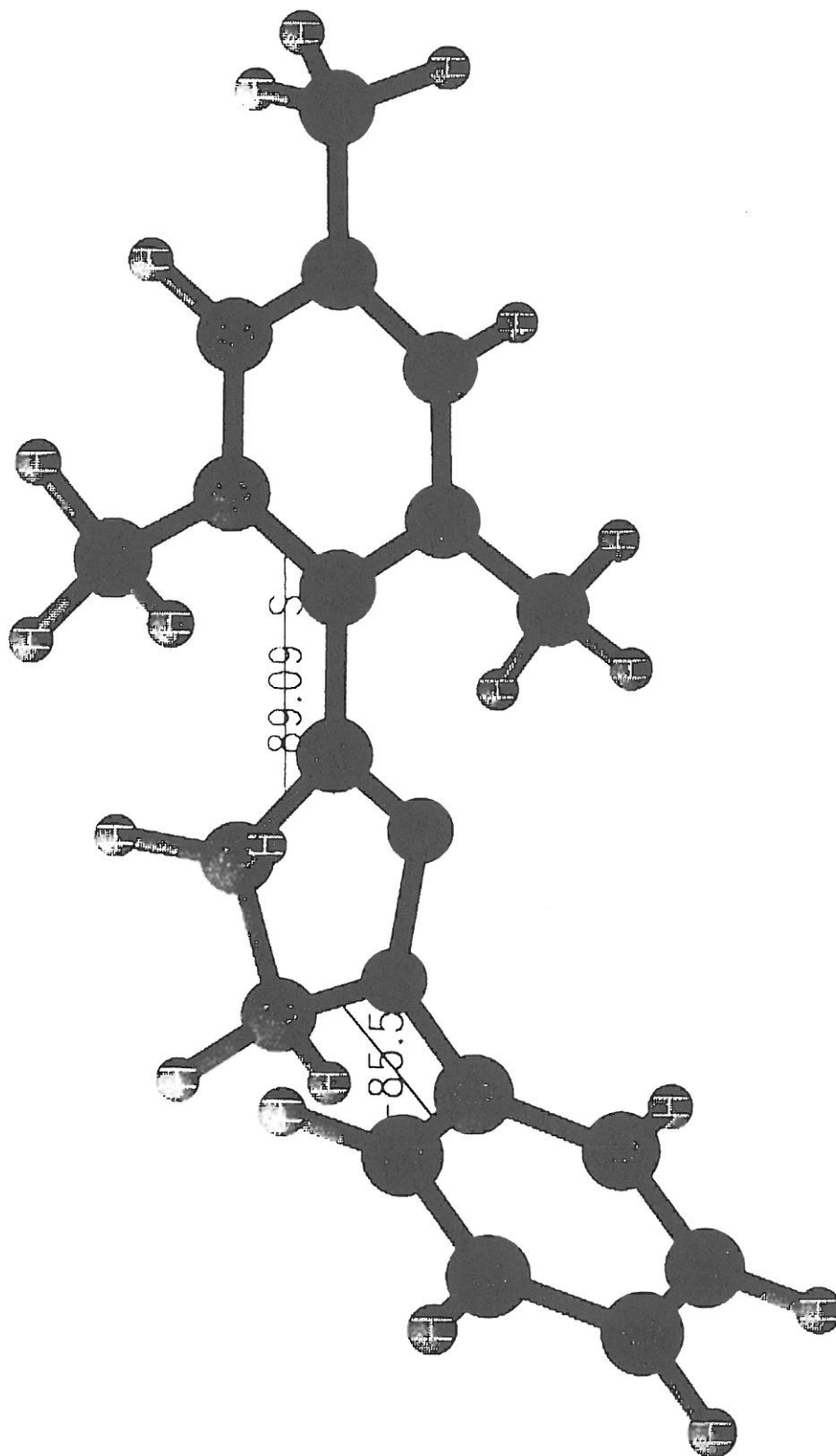


Fig. 13. The Fluorescence and Scintillation Properties of New Oxazoles, Oxadiazoles and Pyrazolines

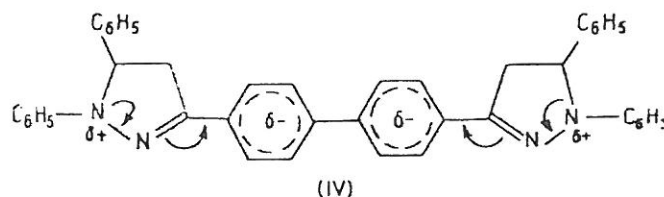
PETER LEGGATE and DERREK OWEN

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1,4-phenylene	PYPYP	244-250	420	3.8	472	498	
4,4'-biphenylene	PYBYP	238-294 (dec.) ^h	408	4.9	465	487	
4,4'-(3,3-dimethylbiphenylene)	dimethyl-PYBYP	240-244	398	6.2	458	480	
1,3,5-triphenyl-2-pyrazoline	PYP ⁱ	136-138	363	1.8	439	—	

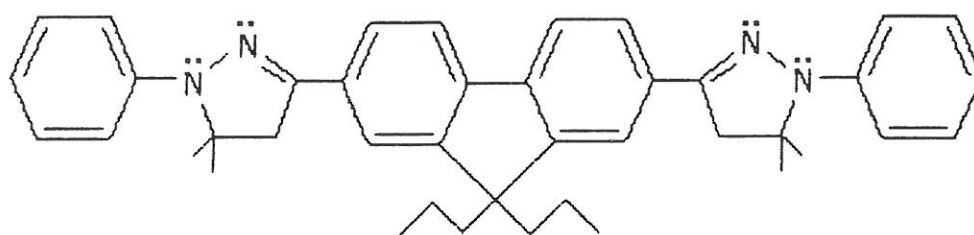
Molecular Crystals, 1968, Vol. 4, pp. 357-373
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Fig. 14. For example, the resonance system of PYBYP may include structures such as (IV) in which a nitrogen atom in each heterocyclic ring acquires a partial positive charge and the residual



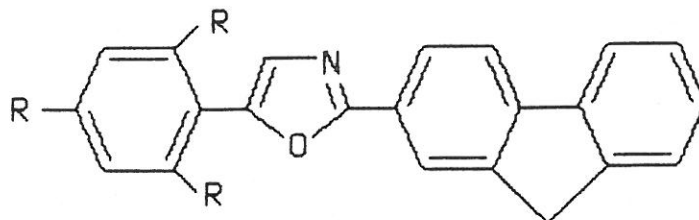
negative charge is distributed on the adjacent carbocyclic ring. In structure (IV) the electronic character of the molecule is analogous to that of two "isolated" triphenylpyrazoline molecules.¹² The extension of the conjugated system separating the two heterocyclic rings will stabilize such isolated structures and increase their contribution to the resonance system. Contributions to the electronic state of the molecule by isolated structures will tend to displace the spectra to shorter wavelengths.

Fig. 15
PHOTOPHYSICAL PROPERTIES OF A NEW DIPYRAZOLINE
WITH FLUORENE CENTER



Solvent	Absorption	Fl. Em.
Cyclohexane	399nm($\epsilon = 32,000$); 333(20,000); 303(23,000); 249(22,000); 215 (41,000)	448nm 475(sh)
Toluene	407 (33,000); 303 (24,000)	472
Ethanol	390 (33,000); 304 (24,000); 247 (22,000) 215 (41,000)	465

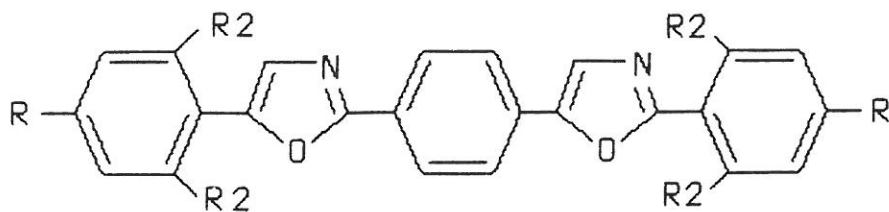
Fig.16. THE "MESITYL" EFFECT ON OXAZOLES



R	Absorption		Fl. Emission
H	361nm	($\epsilon = 23,000$)	418nm
	344	(46,000)	
	333	(41,000)	
	318	(29,000)	
CH ₃	332	(42,000)	410
	320	(46,000)	
	310	(36,000)	

M. D. Barnett, G. H. Daub, F. N. Hayes, D. G. Ott, J. Am. Chem. Soc. 82, 2282 (1960).

Fig.17. THE "MESITYL" EFFECT ON POPOP DERIVATIVES



R	Absorption		Fl. Emission
R = R ₂ = H, POPOP	365nm	($\epsilon = 48,000$)	418nm
R = R ₂ = CH ₃ , MOPOM*	328	(48,000)	410
R = (CH ₃) ₃ C, R ₂ = CH ₃ , DBTeM-POPOP**	328	(45,000)	410

*Synth. only, not pure: A. T. Balaban et al., Revue Roumaine de Chemie 30, 977 (1985). **This work.

Fig. 18

The importance of high extinction coefficient...

...for high emission intensity may be seen in the relation shown in equation:

$$\text{Emission Intensity} = (2.3) (\text{Excitation Intensity})$$

(Optical Path Length) (FQE) (Fluor Conc.) (*Extinction Coefficient*)

- (1) excitation intensity from the gamma source is constant
- (2) path length is constant since all plastic samples used have the same dimensions
- (3) fluor concentrations in terms of number of molecules present (molarity) are held constant
- (4) Fluorescence Quantum Yields (FQEs) vary only from 0.85 to 1.00.

MOLECULAR ELECTRONIC CRITERIA FOR SELECTION OF RADIATION-HARD SCINTILLATORS

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ABSTRACT

Molecular electronic criteria for selection of dopants for radiation-hard scintillator screens are discussed in terms of three categories of fluorescent organic materials: (1) red-spectrum emitters, (2) wavelength-shifters, and (3) radiation-induced fluorescences. For each category the criteria for separation from interfering fluorescences, and radiation and intrinsic photochemical stability are discussed.

1. Introduction

The need for radiation-hard scintillators for high intensity radiation beam research directs attention to special criteria for selection of suitable fluorescence materials. These materials usually are introduced as dilute dopants into plastic scintillator screens. There is a large repository of spectroscopic information on fluorescence of organic molecules, but the radiation-hard scintillator poses unique criteria for selection of suitable dopants. Among the principle ones could be listed (1) *long-wavelength visible emission (green to red)* to minimize interference from intrinsic UV and violet-blue region spurious fluorescences, (2) *wavelength shift effects*, which yield a large "Stokes-shift" to separate the observed emission from the primary absorption region, and (3) *exceptional stability under beam irradiation* and under exposure to atmospheric oxygen in the presence of excitation.

Our presentation will be divided into three principal sections in which various approaches to the principal criteria will be discussed.

2. Red-Spectrum Emitters

A recent massive compendium [1] of "organic colorants" permits selection of fluorescent molecular specimens by a variety of criteria. If we use the criterion of fluorescence emission in the red (near infrared) spectral region, there are whole series of dyes which can be selected. Using the general criterion that high chemical stability, and stability against photo-oxidation should parallel to some degree stability against radiation damage, the list becomes much smaller.

The anthraquinonoid dyes (Fig. 1) constitute a group which could serve as a good example of promising fluorescent materials for radiation-hard scintillators. These are in the category of "vat-dyes," prepared by photo-oxidation from a colorless base form. Presumably as the highest oxidized form, these should be stable against further oxidation degradation,

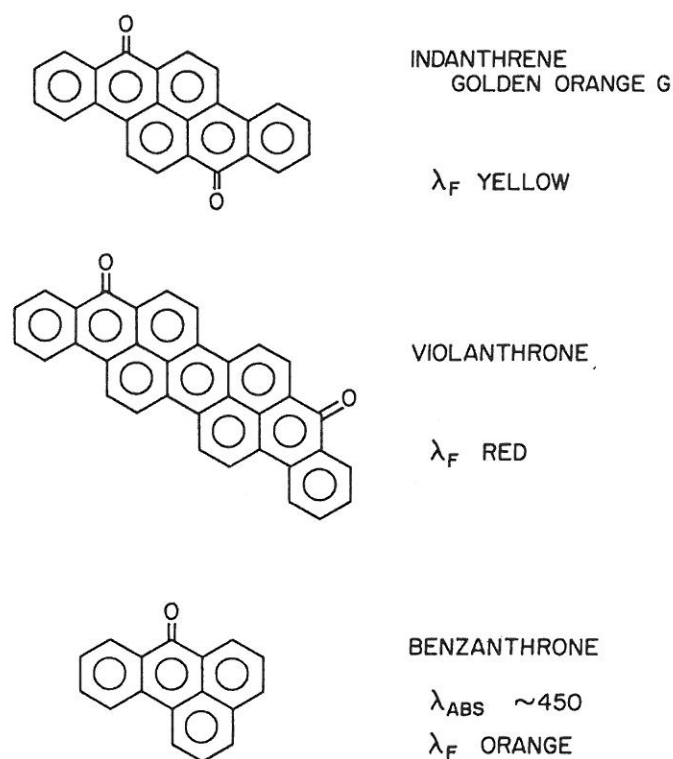


Fig. 1. Anthraquinonoid Vat Dyes

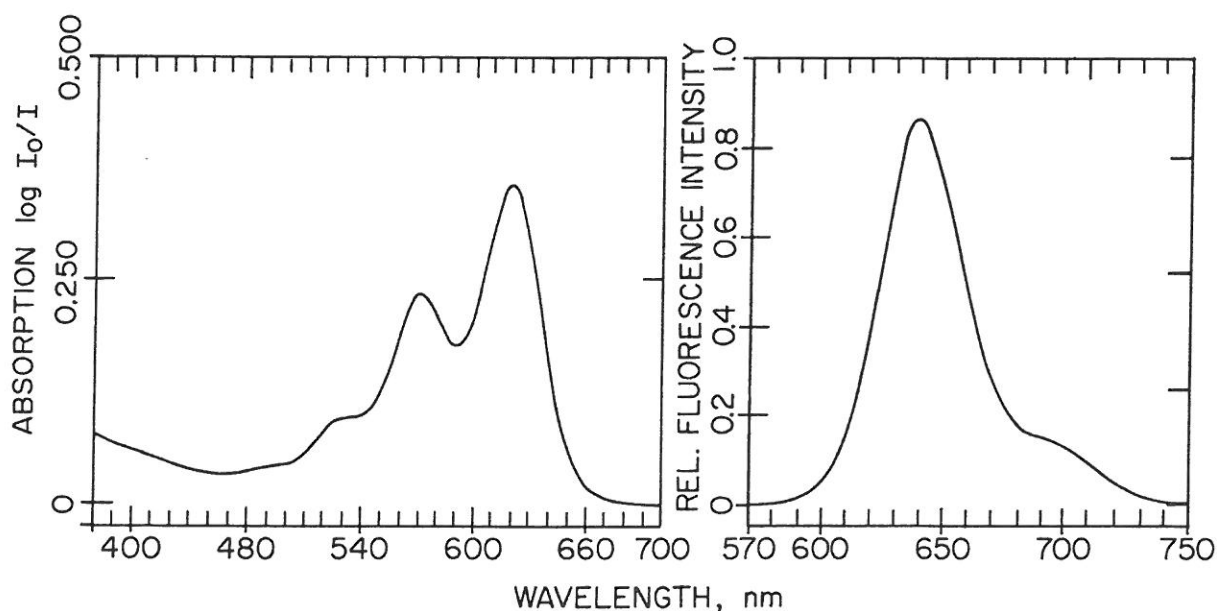


Fig. 2. Violanthrone spectra in 1-chloronaphthalene at 298 K

especially considering the harsh condition of formation of the colored form. They are generally of exceptional thermal stability. The absorption spectrum of violanthrone is given in Fig. 2. The fluorescence quantum yield is rather high, and a beautiful red fluorescence

is observed. A red fluorescence is generally advantageous in scintillator filters separating the emission from all UV interferences. However, the relation of the fluorescence envelope to the absorption envelope suggests that there should be a very strong self-absorption on the short wavelength side of the fluorescence. In the present case the shape of the fluorescence envelope shows that certainly no self-absorption is present (a vertical onset of fluorescence would have appeared). The explanation is that the solution used was very dilute, and the fluorescence observation technique (right angle or front-face excitation) would minimize self-absorption.

Solubility of this large molecule is limited in most ordinary organic solvents. The solvent 1-chloronaphthalene is a good solvent for violanthrone and other large polycyclic quinones. Presumably one could introduce a dopant via a solution in such a solvent added to, e.g., polystyrene monomer, incorporating the violanthrone in this manner in the polymer screen.

Phthalocyanines offer another category of red-spectrum fluorescent dyes, provided that metallo-phthalocyanines with paramagnetic or heavy atoms are avoided (fluorescence is quenched in these, the excitation appearing as still longer wavelength phosphorescence) [1].

3A. Wavelength-shifters: Proton-transfer Fluorescence

A *wavelength-shifter* is defined here as a molecular system which exhibits a *large separation of fluorescence peak or region versus the normal absorption onset, peak, or region*. An absorption corresponding to the shifted fluorescence must be absent, and self-absorption of the fluorescence is then negligible. Wavelength shifts corresponding to energy losses (through vibrational relaxation) of 5000 to 15000 cm^{-1} are observed in numerous molecular systems, but only if a great electronic rearrangement or large molecular skeletal configurational change occurs. It can be stated then that the emitting species is chemically distinguished from the absorption species. In spectroscopic language then it would be anomalous to call the observed wavelength shift a "Stokes-shift," since that term implies that the absorbing species and the emitting species are chemically identical. Large Stokes shifts are observed via dielectric relaxation solvent effects on certain molecules, but such shifts are much smaller ($<3000 \text{ cm}^{-1}$) than those which are found in true wavelength shifters.

We shall describe two molecular excitation phenomena which yield *wavelength-shifters*: excited state intramolecular proton transfer (ESIPT or simply PT) (Section 3A), and twisting-intramolecular-charge-transfer (TICT) (Section 3B).

The most dramatic case of wavelength-shifter fluorescences occur as a result of the intramolecular proton-transfer phenomena. [2] This has expanded into such a widely-studied field [3], and offers such a variety of cases, that some details will be explored as general background. Certainly 3-hydroxyflavone (3-HF) has attracted the most diverse attention on the part of researchers, starting with the first report [2] of its huge "Stokes-shift" of some 10000-12000 cm^{-1} from its primary absorption (Fig. 3).

The origin of the large wavelength shift can be understood in terms of the electronic structural change in the molecular skeleton, upon the excitation-induced proton-flip (Cf. Fig. 4). The normal molecule (S_0) structure possesses an -OH group internally (and weakly) "hydrogen-bonded" to the adjacent -C = O group. In the excited electronic state (S_1) electronic density changes strongly favor a proton-flip, with the covalent bond now forming

between the -H and the O atom of what had been the $-C=O$ group. The molecule becomes "fully aromatic," with the unusual *pyrylium* ring containing an aromatic ring oxygen (Fig. 4).

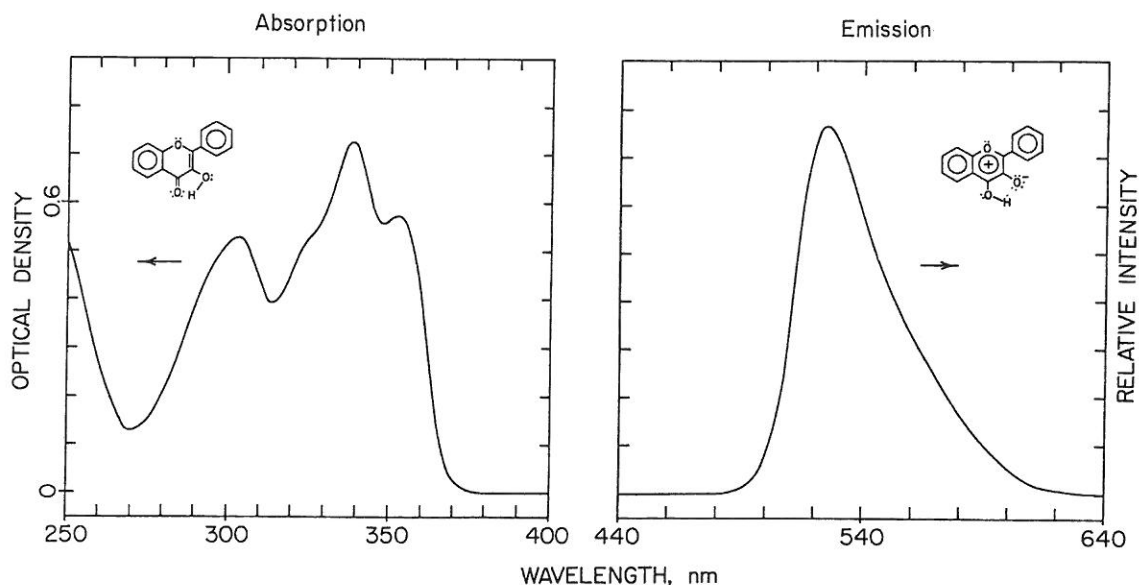


Fig. 3. Spectra of 3-hydroxyflavone (3-HF) in cyclohexane at 298 K

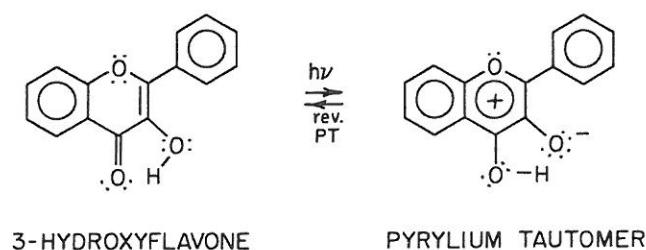


Fig. 4. Normal and tautomer forms of 3-HF

Schematic potential energy curves (Fig. 5) illustrate the excitation energetics of the intramolecular proton transfer. It is known that the rate of the $S_1 \rightarrow S_1'$ (PT) process is on the order of picoseconds. However, The $S_1' \rightarrow S_0'$ fluorescence (the "proton-transfer" green fluorescence (F_2) observed at 525 nm in 3-HF) is a nanosecond range normal fluorescence, but obviously must occur at a much longer wavelength than what would be expected as the $S_1 \rightarrow S_0$ fluorescence corresponding to the normal absorption. The $S_1 \rightarrow S_0$ violet fluorescence (F_1) can be observed under certain solvent perturbation conditions [4]. In addition, picosecond transient absorption spectroscopy permits study of the $S_0' \rightarrow S_1'$ and $S_1' \rightarrow S_2'$ absorptions [5]. However, it is clear from the potential curves of Fig. 5 and the spectral curves of Fig. 3 that there is no absorption in the large gap between the UV absorption onset at 340 nm and the proton-transfer fluorescence onset at 500 nm. Thus, self-absorption of the latter fluorescence is absent, as the S_0' state depopulates in about 30 psec.

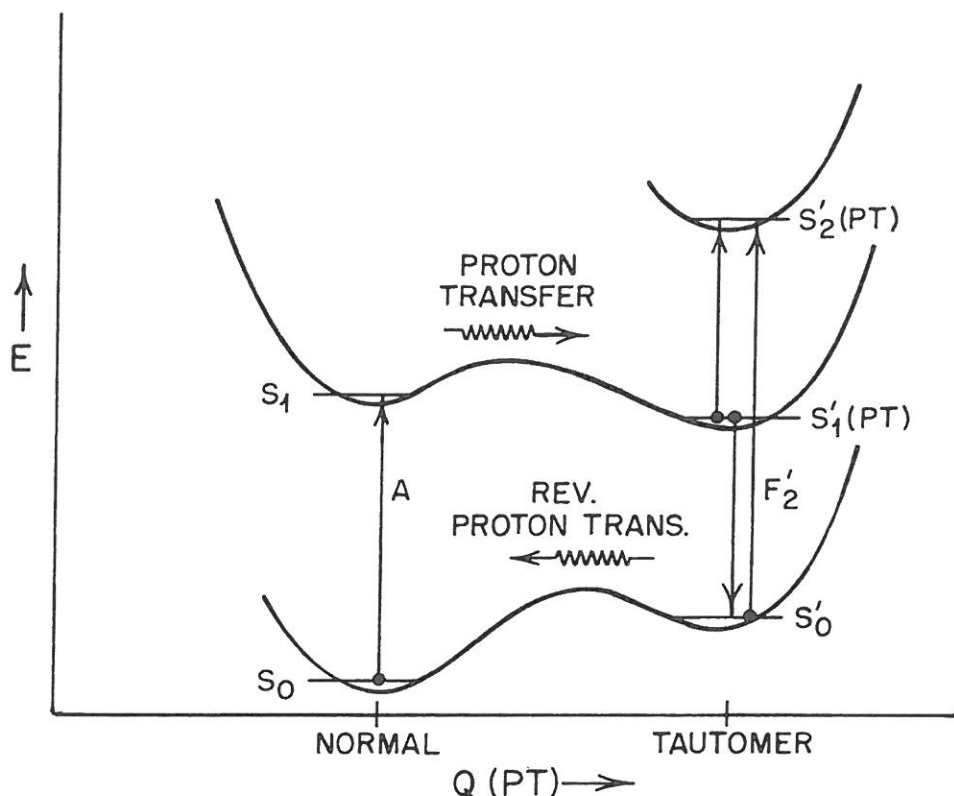


Fig. 5. Proton-transfer potentials

A case of *wavelength-shifting proton-transfer fluorescence*, which also is a *red-spectrum emitter* would offer a double advantage. Such a case is found in 2-hydroxy-5,6-naphthotropone (HNT) (Fig. 6), an unsymmetrical proton-transfer case [6] in which the two possible tautomers are distinguishable. In symmetrical 2-hydroxytropone (tropolone) the two tautomers are indistinguishable, and the spectroscopic observation is merely a proton-tunneling splitting on the order of tens of cm^{-1} , seen only in high-resolution spectroscopy.

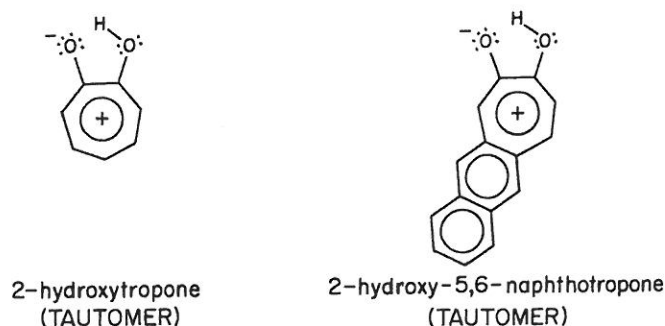


Fig. 6. Structures of hydroxytropones

The proton-transfer fluorescence spectrum for HNT is given in Fig. 7. A strong red fluorescence of short lifetime is observed. Information on photochemical stability and

radiation stability of this species is not yet available. Many chemical variations of their structural type can be envisaged.

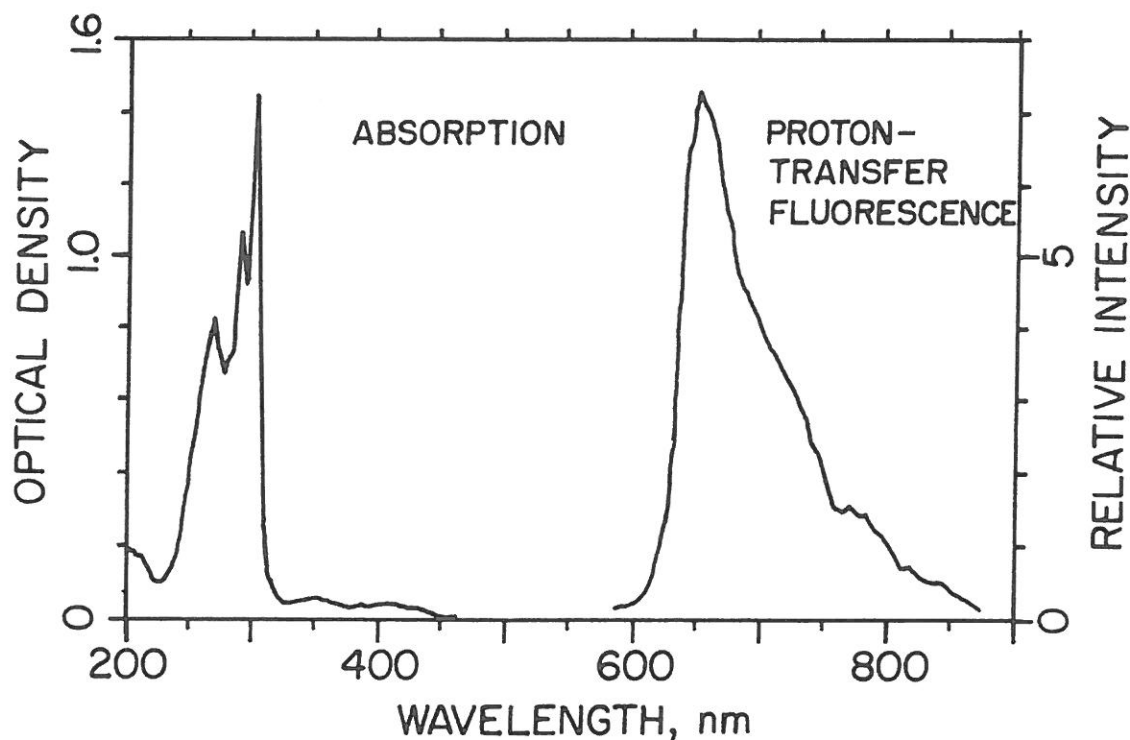


Fig. 7. Spectra of HNT (2-hydroxy-5,6-naphthotropone) in cyclohexane at 298 K

Another outstanding example of a proton-transfer fluorescence approaching the red region is provided by 2,2'-bipyridyl-3-ol (Fig. 8), on which extensive researches by Grabowska and co-workers have been published together with related molecules [7]. Their absorption and fluorescence spectra are shown in Fig. 9. The energy loss gap observed is 6000 cm^{-1} , with a peak-to-peak shift of 11500 cm^{-1} (sometimes considered as a "Stokes shift").

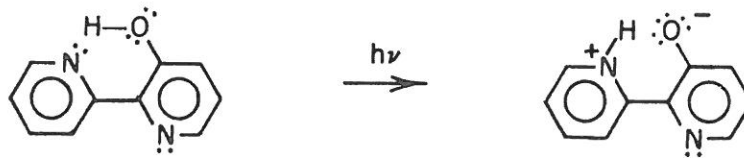


Fig. 8. Proton-transfer in 3-hydroxy-2,2'-bipyridyl

A similar example is that of the somewhat complicated molecules also studied by the Grabowska group in Warsaw, the benzoxazolyl compounds [8]. The double-proton-transfer case (2,5-bis(2-benzoxazolyl)hydroquinone shows a first absorption max at 24000 cm^{-1} (onset 22500 cm^{-1}), and a double-proton-transfer fluorescence max at 16000 cm^{-1} (onset 18000 cm^{-1}), with an energy-loss band-gap of 4500 cm^{-1} (peak-to-peak shift of 8000 cm^{-1}). The examples

of intramolecular proton-transfer fluorescence studied by the Grabowska group offer some excellent examples of yellow-to-red fluorescence emission; the photo-stabilities and radiation stabilities have yet to be determined. In the overview paper on research in proton-transfer spectroscopy [3] numerous other examples are cited, but most of them would seem to offer no advantages over 3-HF. A special issue of *Chemical Physics* featuring proton-transfer spectroscopy and dynamics has been published recently [9], citing many other cases.

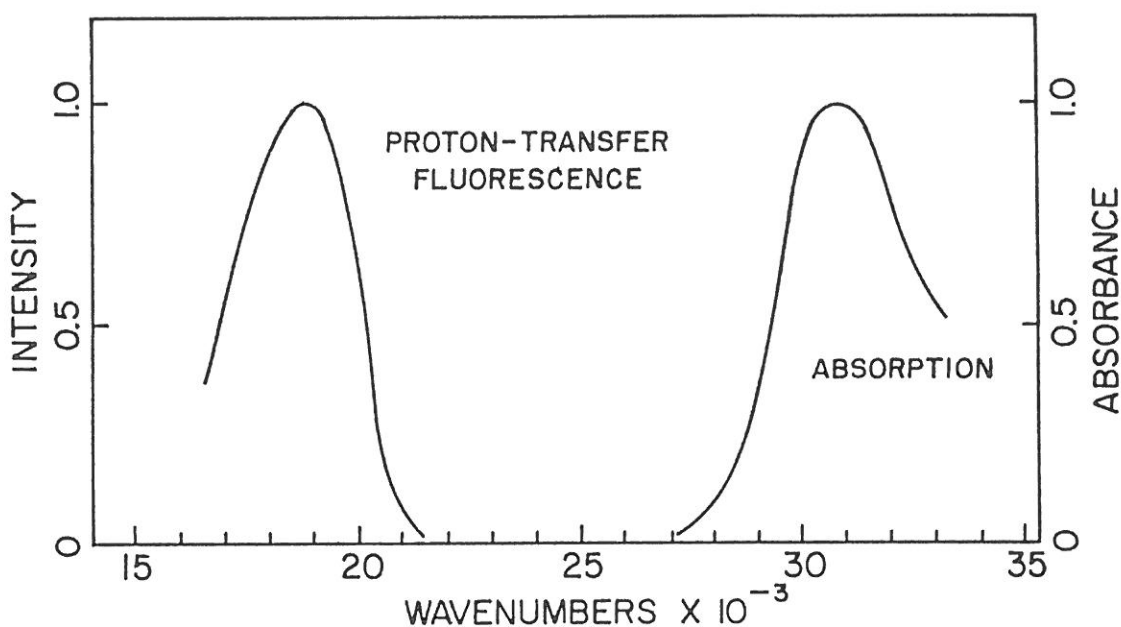


Fig. 9. Spectra of 2,2'-bipyridyl-3-ol in hydrocarbon glass at 77 K

As research on radiation stability develops, it should be possible to engineer chemical structures which feature the desirable properties of red-spectrum fluorescence, large wavelength shift, and intrinsic radiation and photostability.

3B. Wavelength-shifters: TICT State Fluorescence

In some molecular systems a novel origin of dual-fluorescence has been observed. In Warsaw, Z. Grabowski and co-workers [10] have made the keynote interpretation in appropriate cases as a wavelength-shifted fluorescence arising from *twisting-intramolecular-charge-transfer* (TICT) states as the origin of the second fluorescence.

Fig. 10 diagrams the origin of this phenomenon, in a further elaboration [5] based on theoretical computation of Murrell and co-workers [11]. In a molecule capable of undergoing a bond-torsion or twisting, at co-planarity (0°) a normal sequence of states may exhibit a second excited state of charge-transfer (CT) type (e.g., aromatic -NH_2 or aromatic $\text{-N(CH}_3)_2$ molecules). Upon excitation, torsional relaxation of the CT state leads to an avoided crossing with the potential of the first excited state. In a dielectric medium of high dielectric constant, the twisting-CT state (TICT) may be pulled below the minimum of the first excited state.

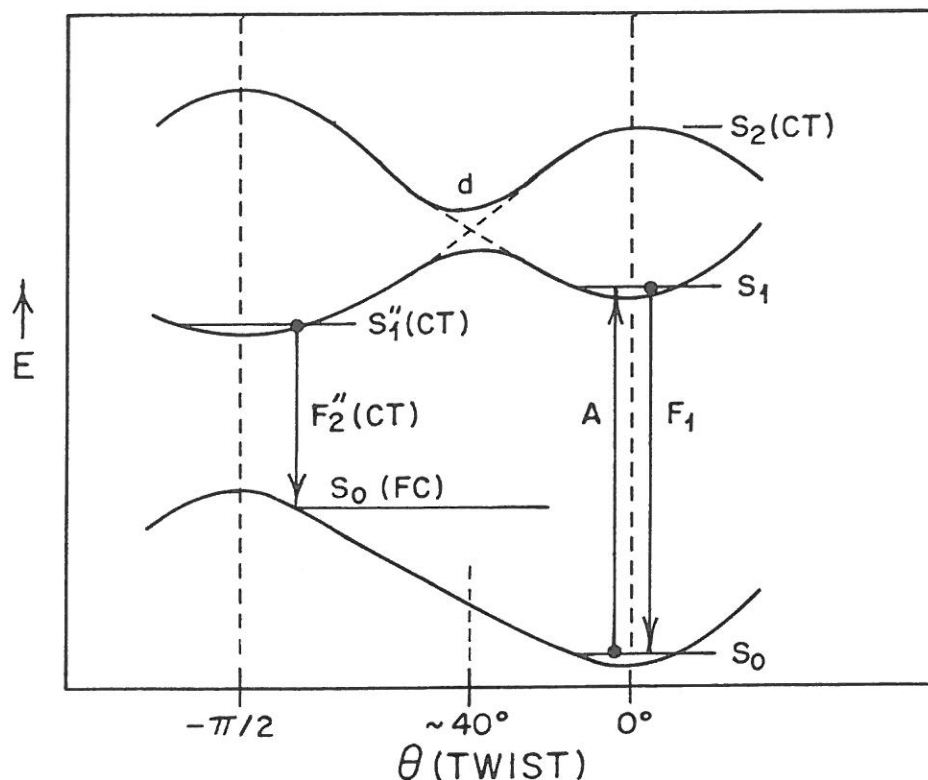


Fig. 10. Twisting-intramolecular-charge-transfer (TICT) potentials with non-crossing region offering an adiabatic path from $S_1 \rightarrow S_1''(\text{CT})$

In a molecule with TICT-states under dielectric relaxation, after absorption (A), both normal (F_1) and TICT state fluorescence (F_2'') may be observed. The benzanilide and N-methylbenzanilide molecules (Fig. 11) offer somewhat complex examples of TICT-state fluorescence [5]. The absorption spectra for these molecules is in the middle UV, Fig. 12, whereas the dominant fluorescence occurs in the blue-green region. The benzanilide long wavelength fluorescence proves to consist of both proton-transfer and charge-transfer components [5]. In this case the proton-transfer ($-\text{NH}$ to $\text{O}=\text{C}-$) requires a molecular H-bonded dimers to form, accessible only in hydrocarbon solvent.

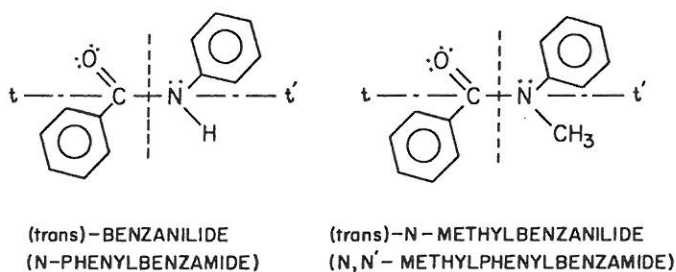


Fig. 11. Structures of benzanilides

For our purpose, the N-methylbenzanilide is of more direct interest. The wavelength-shifted band (Fig. 12) is purely of CT type, and is very sensitive to dielectric constant of the medium. Can this be used as a wavelength-shifter for scintillation screens? It is clear that if the torsional motion is inhibited, the TICT-state fluorescence would be unobservable. Our work to date compares only fluid solutions (F_2'' , a TICT-state emission dominant) to rigid glass solvents (frozen alcohols, etc.) in which the TICT-state fluorescence is absent, normal fluorescence F_1 reappearing. How the TICT-state phenomenon will be affected by polymeric matrix incorporation will be a question of internal motion in various polymers.

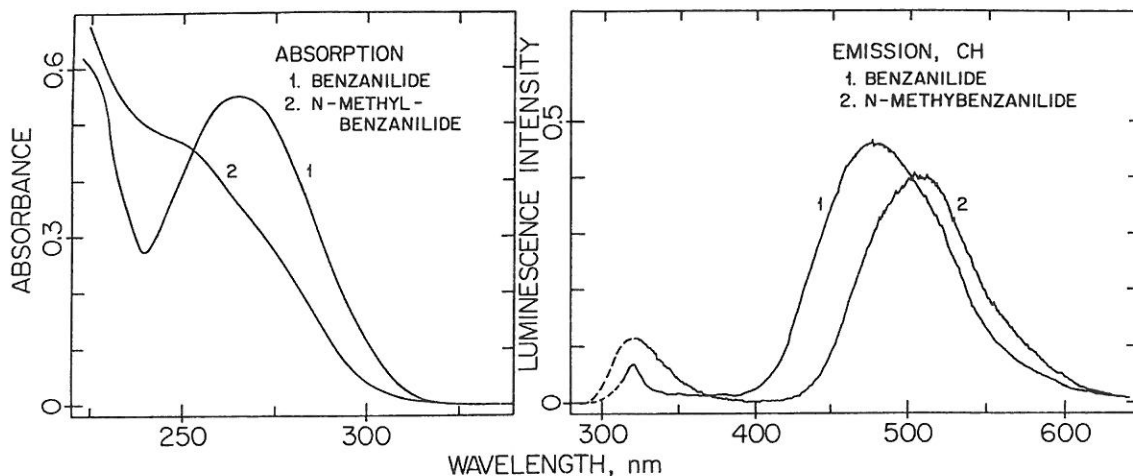


Fig. 12. Spectra of benzanilides in cyclohexane at 298 K

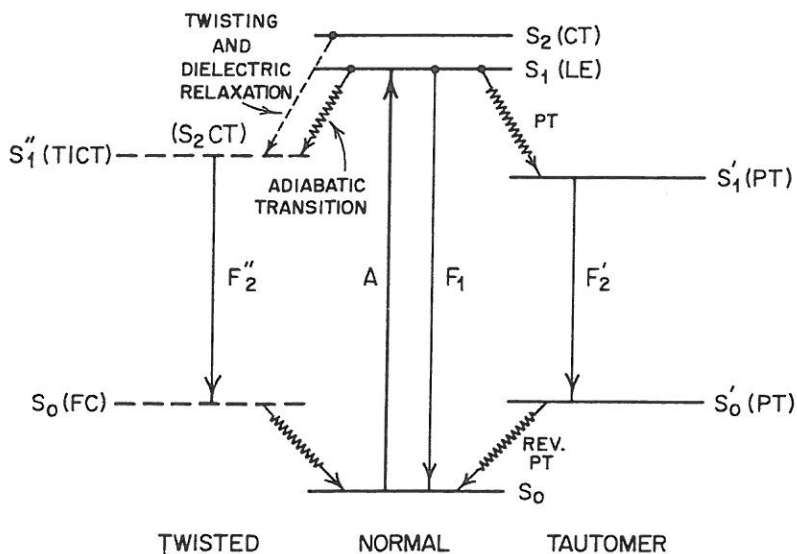


Fig. 13. Triple fluorescence competition: F_1 normal, F_2' proton transfer, F_2'' twisted charge transfer

The important point about TICT-state emissions is that they may offer undesired competition to the wavelength-shifts observed as proton-transfer fluorescence. Fig. 13

summarizes the problem of triple fluorescence competition. Spectroscopists can readily predict whether TICT-state or PT-state fluorescence can be observed, either serving as major wavelength-shifters. But the triple-fluorescence competition must be avoided; only recently has this possibility become evident [5].

4. Radiation-induced Fluorescences as Scintillators

Upon irradiation with strong UV beams, X-rays, and radiation sources a new fluorescence may appear, in some cases replacing a normal fluorescence, or in others yielding a fluorescent molecular species from a non-fluorescent precursor.

A remarkable example of this behavior is the molecule 1-naphthylamine (Fig. 14). This molecule has intrinsically a near-UV absorption deep violet fluorescence. Upon strong irradiation with an intense UV beam (302 nm) an intense red fluorescence is generated, with an unusually structured fluorescence envelope (Fig. 15). This could be excited by the new absorption band at 365 nm generated by the photo-irradiation.

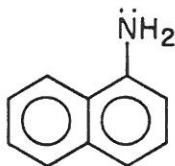


Fig. 14. Chemical structure of 1-naphthylamine

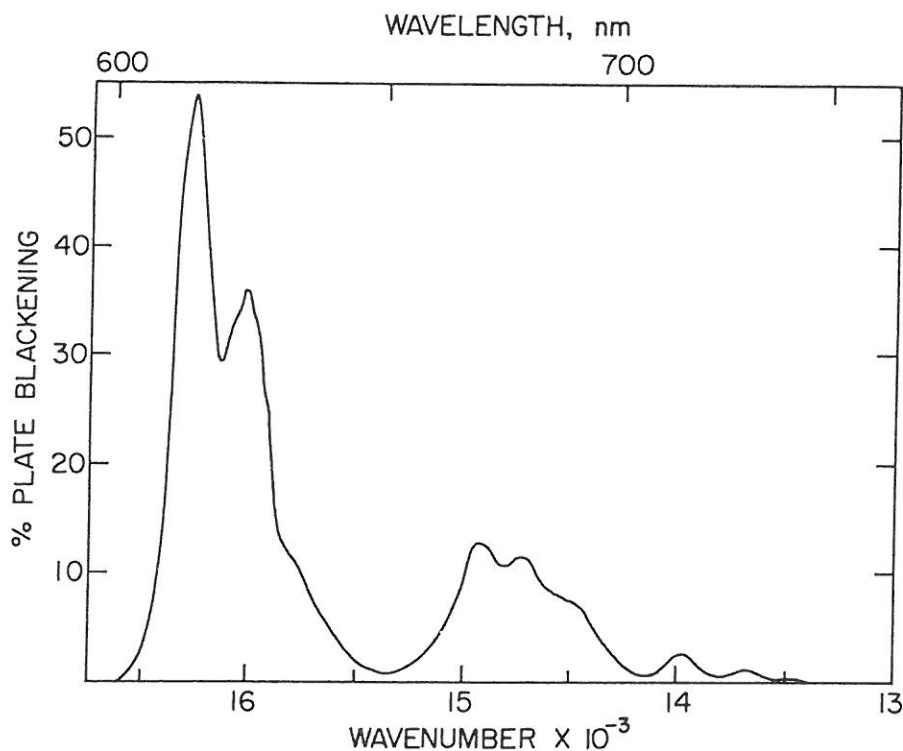


Fig. 15. Photo-induced fluorescence of 1-naphthylamine in hydrocarbon glass matrix at 77 K

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The isomer 2-naphthylamine showed analogous photo-induced red fluorescence, but the excitation beam required 280 nm UV, and the excitation of the red fluorescence required 302 nm UV.

The experiments on the naphthylamines were performed on the solutes in dilute solution in hydrocarbon glasses as a rigid solvent matrix. Preliminary work indicates that the red fluorescence *requires* the presence of dissolved O₂ as the electron-trapping agent for the naphthylamine ion-radical production to which the red-fluorescence is attributed. The red-fluorescing species is perfectly stable with time as long as the rigidity of the matrix is maintained.

Such radiation-induced fluorescences may be an ideal approach to radiation-hard scintillator development. There is an old physics literature on this subject [12], in which crystalline and solution samples were pre-irradiated with UV, X-rays, and electron beams in order to produce a *Hauptspektrum* as compared with what the researchers considered a *Vorspektrum*. There is considerable experience among spectroscopists and photochemists with such radiation-induced photo-oxidation phenomena. These may offer one of the best paths of research for new radiation-hard scintillators.

Acknowledgement

The authors are pleased to acknowledge the contribution of Renschler and Harrah [13], who used (unwittingly) our discovery of the proton-transfer fluorescence of 3-HF as wavelength-shifters in developing scintillator screens.

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