2-(2'-Hydroxyphenyl)benzothiazoles, -benzoxazoles, and -benzimidazoles for Plastic Scintillation Applications[†]

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A new series of fluorescent compounds has been tested as dopants for plastic scintillation applications. Several 2-(2'-hydroxyphenyl)benzothiazole, -benzoxazole, and -benzimidazole derivatives have been prepared and studied in a polystyrene matrix. Each derivative has been added to a styrene solution which has been thermally polymerized. The transmittance, fluorescence, and light yield characteristics of these compounds in polystyrene have been determined. Their emission time distributions have also been measured, and the decay time constants have been calculated from these data. In addition, the doped polystyrene samples have been irradiated to a total dose of 10 Mrad, utilizing a ^{60}Co source in order to evaluate their susceptibility to radiation-induced damage.

Introduction

Certain materials emit light when they interact with nuclear particles or electromagnetic radiation. Particle detectors based on this scintillation property have been used for many years in nuclear and high-energy physics experiments. Among the materials utilized for these detectors, scintillating plastics are noteworthy for their fast response and ease of manufacture. New applications for plastic scintillation detectors have been made possible after recent developments in both scintillating plastic optical fibers and photon detection devices.[1] The renewed interest in plastic scintillators has encouraged research toward the modification and improvement of their fundamental properties, namely light yield, decay time, and radiation resistance.

Standard plastic scintillators fluoresce in the blue region of the visible light spectrum and consist of a polymer matrix doped with two fluorescent organic compounds. Polystyrene and poly(vinyltoluene) are common materials utilized as the polymer base. The fluorescent compounds are generally referred to as the primary and secondary dopants. Recent technological developments have enabled the use of new polystyrene-based scintillating and wavelength shifting (only a secondary dopant present) fibers whose emissions range from the green to the red region of the visible spectrum. The scintillation mechanism involves three main processes.[2] First, ionizing particles passing through the scintillator excite the polymer molecules. The concentrations of the primary and secondary dopants are sufficiently small to neglect their direct excitation. Shifting of the π-electrons into excited singlet states is the major excitation process. Second, energy is transferred from the excited state of the polymer to the primary dopant through the Förster mechanism.[3] This process is described by a dipole–dipole interaction in which a nonradiative energy transfer occurs between the first excited π-singlet state of the polymer and the primary dopant. This is a very efficient process which does not depend upon the polymer radiative quantum yield. Third, the primary dopant transfers its excitation energy to the secondary dopant through the emission and reabsorption of a photon. The overall process generates photons of longer wavelength than those that would have been emitted by the excited polymer molecules in the absence of any dopants.

The use of plastic scintillators emitting at longer wavelengths has been dictated by the results from numerous radiation damage tests. These studies indicate that the optical properties of polystyrene degrade with exposure to ionizing radiation.[4–7] This effect is observed as an increase of its absorption region toward longer wavelengths and is responsible for losses in the light output of the detector. Since the radiation-induced damage causes the absorption of polystyrene to extend up to 500 nm, the light emitted by the standard dopants is partially reabsorbed, resulting in the observed light yield loss of the detector. New dopants fluorescing at wavelengths longer than 500 nm yield a plastic scintillator less susceptible to radiation damage.

Among the new fluorescent compounds tested, 3-hydroxyflavone (3HF) has been found to be an excellent candidate for green-emitting plastic scintillators.[8,9] Its absorption and emission peaks are at approximately 350 and 530 nm, respectively. The large separation between absorption and emission spectra is due to an excited-state intramolecular proton transfer that occurs when 3HF is excited by UV or ionizing radiation. Many 3HF derivatives have been prepared in an attempt to modify the spectroscopic characteristics to the needs of different detectors.[10–12] Another fluorescent compound which also

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[†] Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday.

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Table 1. List of Compounds Studied[a]

X	R_3	R_4	R_5	name	yield[b] (%)	method[c]
S	H	H	H	HBT[d]		
S	Cl	H	H	3CHBT	45	A
S	H	H	Cl	5CHBT	49	A
S	H	MeO	H	4MOHBT	32	A
O	H	H	H	HBO[d]		
O	Cl	H	H	3CHBO	10	A
O	H	H	Cl	5CHBO	63	B
O	H	Ph	H	4PHBO	43	B
NH	H	H	H	HBI	30	B
NH	Cl	H	H	3CHBI	75	B
NH	H	H	Cl	5CHBI	20	B
NH	H	Ph	H	4PHBI	63	B

[a] See Figure 1 for a general structure of the compounds. [b] Reaction yield. [c] Synthetic method used. [d] Commercially available.

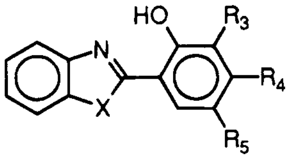

Figure 1. Substitution pattern in HBT, HBO, and HBI.

exhibits excited-state intramolecular proton transfer is 2-(2′-hydroxyphenyl)benzothiazole (HBT). Its absorption and emission wavelengths are similar to those of 3HF, but low quantum yield and questionable radiation resistance render this compound unsuitable for plastic scintillation applications. Nonetheless, HBT remains of interest because 3HF presents problems of oxidation and UV/visible-induced degradation[13] which do not seem to affect the HBT molecule. Different HBT derivatives prepared with the aim of solving these intrinsic drawbacks have met with moderate success.[14] Other compounds such as derivatives of 2-(2′-hydroxyphenyl)benzoxazole (HBO)[15] and 2-(2′-hydroxyphenyl)benzimidazole (HBI)[16] are being investigated.

The photophysical characteristics in polystyrene and a radiation damage study of a new set of HBO and HBI derivatives prepared at Fermilab are reported here. These results are compared to those of HBT and representative HBT derivatives. Table 1 presents the list of the compounds studied. Figure 1 shows a schematic diagram of their molecular structure.

Results and Discussion

The HBT, HBO, and HBI derivatives studied exhibit excited-state intramolecular proton transfer (ESIPT) upon excitation by UV or ionizing radiation. Figure 2 illustrates this mechanism in the HBT molecule.[17-19] The proton transfer causes a structural rearrangement, which is indicated by the large separation between the absorption (λ_{max} = 340 nm) and the fluorescence (λ_{max} = 530 nm) bands. The proton transfer is favored because of an increase in the N-basicity and the O-acidity in the excited state and, in addition, it is aided by a preexisting hydrogen bond. The first compounds prepared at Fermilab were the HBT derivatives. Radiation damage studies performed on scintillator samples doped with these derivatives indicated the formation of a new and permanent absorption band at longer wavelengths. Figure 3 presents these results for two polystyrene samples doped with different concentrations of HBT in order to observe, in more detail, the effect of ionizing radiation (γ-rays) on the HBT molecule. Excitation of this second absorption band, which is clearly distinguished in the higher concentration sample, yields a fluorescence spectrum of distribution and wavelength range similar to those of HBT.[14] However, the lack of separation between absorption and fluorescence bands indicates that it does not involve ESIPT; the proton is already on the N atom. Therefore, this new absorption band has been assigned to the the trans-keto isomer[14,20] formed during irradiation. The presence of this isomer reduces the effective separation between absorption and emission spectra after irradiation and causes light yield losses due to self-absorption.

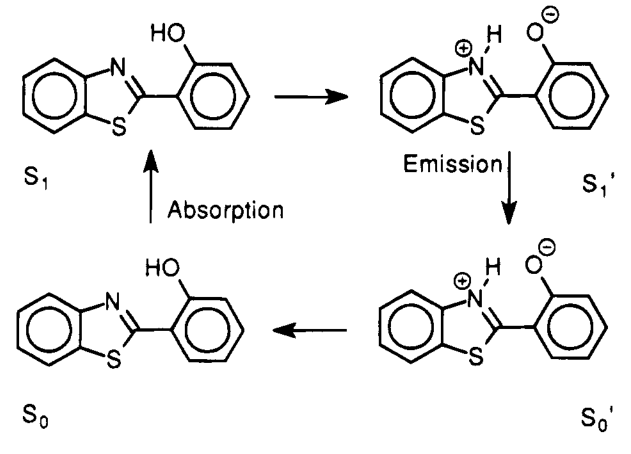

Figure 2. Excited-state intramolecular proton transfer process for HBT.

The HBO and HBI derivatives were synthesized in an attempt to find a compound that would still exhibit ESIPT but would not form isomers under radiation. Figure 4 shows the transmittance and fluorescence spectra for the parent compounds (HBT, HBO, and HBI). Table 2 lists the photophysical characteristics of the compounds studied, including representative HBT derivatives and 3HF for a base reference, since it is a widely used dopant. The polystyrene samples outlined in Table 2 contain 1.25% (by weight) *p*-terphenyl (PT) as the primary dopant. The ESIPT compounds are tested as secondary dopants. Their function is to shift the light from the emission wavelength of PT, λ_{max} = 350 nm, to longer wavelengths. The concentration of the secondary dopant typically ranges from 0.01% to 0.2% (by weight) and depends upon the degree of coupling between the emission distribution of the primary dopant and the absorption curve of the secondary dopant. The objective is to maximize the absorption of the light emitted by the primary dopant.

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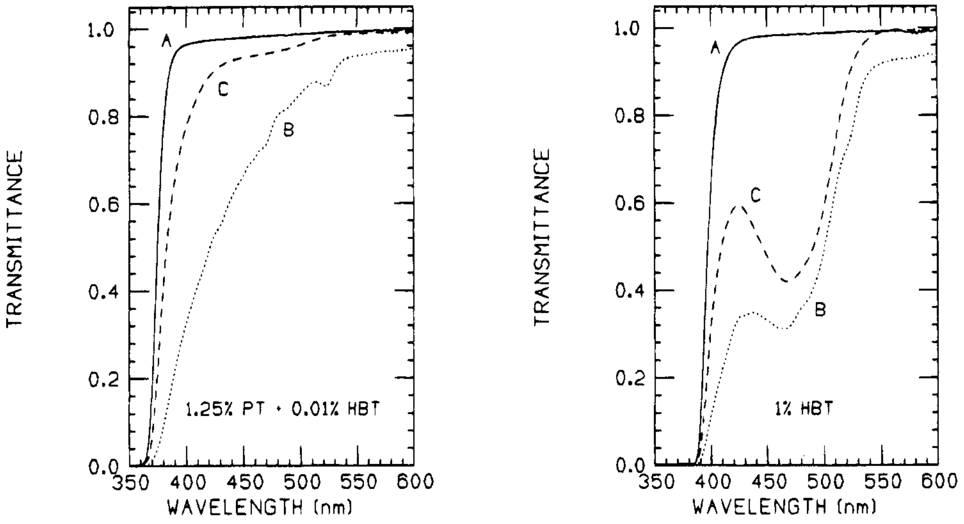

Figure 3. Irradiation of HBT-doped polystyrene samples: (A) before irradiation; (B) after 10 Mrad; (C) after oxygen annealing.

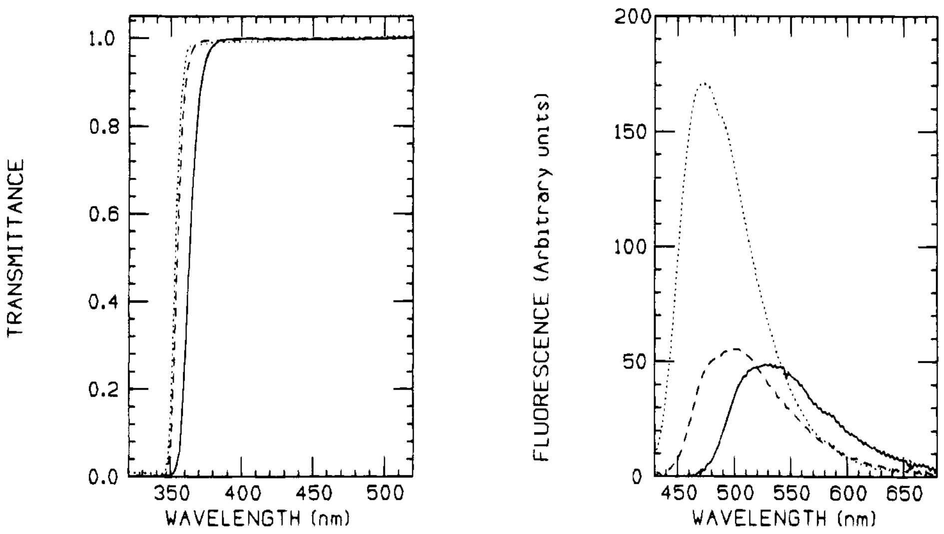

Figure 4. Transmittance and fluorescence spectra of 1.25% PT + 0.01% HBT (solid lines), 1.25% PT + 0.01% HBO (dashed lines), and 1.25% PT + 0.01% HBI (dotted lines).

Table 2. Photophysical Characteristics of the Derivatives in Polystyrene

compd[a]	$\lambda_{abs}{}^{b}$ (nm)	ϵ^{c} (L mol^{-1} cm^{-1})	$\lambda_{em}{}^{d}$ (nm)	rel[e] light yield	decay time[f] τ (ns)
0.01% 3HF	350	15 000	530	1.0	8.5
0.01% HBT	340	15 000	530	0.4	3.9
0.01% 3CHBT	344	16 000	540	0.6	4.8
0.01% 5CHBT	350	17 000	542	0.6	4.8
0.01% 4MOHBT	342	23 000	550	0.4	3.7
0.01% HBO	330	16 000	498	0.4	3.6
0.01% 3CHBO	332	14 000	510	0.6	4.2
0.01% 5CHBO	340	15 000	510	0.7	5.1
0.01% 4PHBO	340	30 000	510	0.8	4.8
0.20% HBI	330	18 000	470	1.1	5.2
0.20% 3CHBI	332	20 000	480	1.1	5.6
0.20% 5CHBI	340	21 000	490	1.2	6.2
0.20% 4PHBI	340	26 000	490	1.1	4.7

[a] Samples contain 1.25% PT as primary dopant. [b] Maximum absorption wavelength (from measurements using diluted styrene solutions). [c] Absorptivity coefficient (from measurements using diluted styrene solutions). [d] Maximum emission wavelength. [e] Light yield values relative to 3HF (from measurements using 334-nm excitation wavelength). [f] A filter was used to remove nonabsorbed light from PT.

The absorption and emission curves of the HBO and HBI derivatives show a hypsochromic shift with respect to those of the HBT derivatives. In the absorption spectra, the shift is approximately 10 nm toward shorter wavelengths, and in the fluorescence spectra, it is about 30 nm for HBO derivatives and 60 nm for HBI derivatives. These spectral differences were anticipated, although the Stokes-shift reduction of the HBI derivatives was not expected to be as significant. Fluorescence measurements were performed using a 334-nm excitation wavelength. The emission spectrum was integrated over all wavelengths to estimate the relative quantum yield of each compound. Light yields were calculated relative to 3HF, since its light output is the highest among the

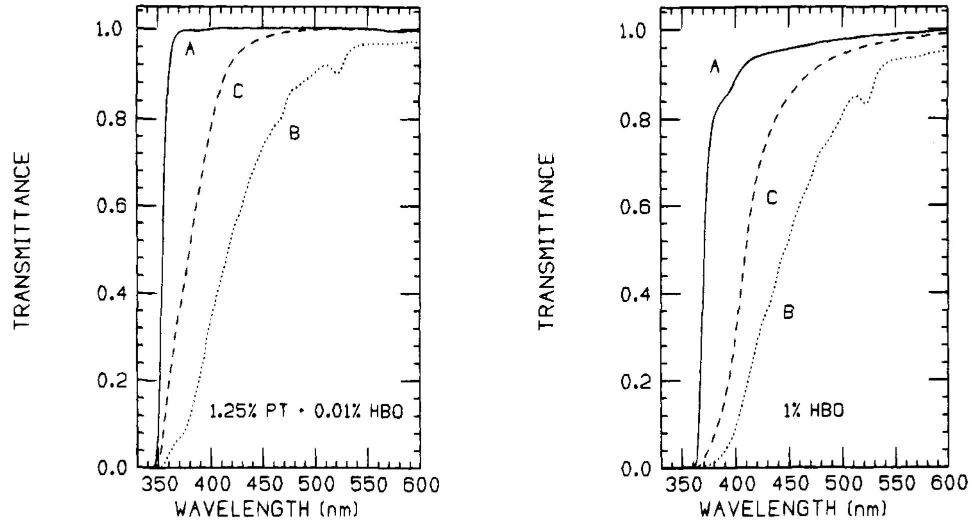

Figure 5. Irradiation of HBO-doped polystyrene samples: (A) before irradiation; (B) after 10 Mrad; (C) after oxygen annealing.

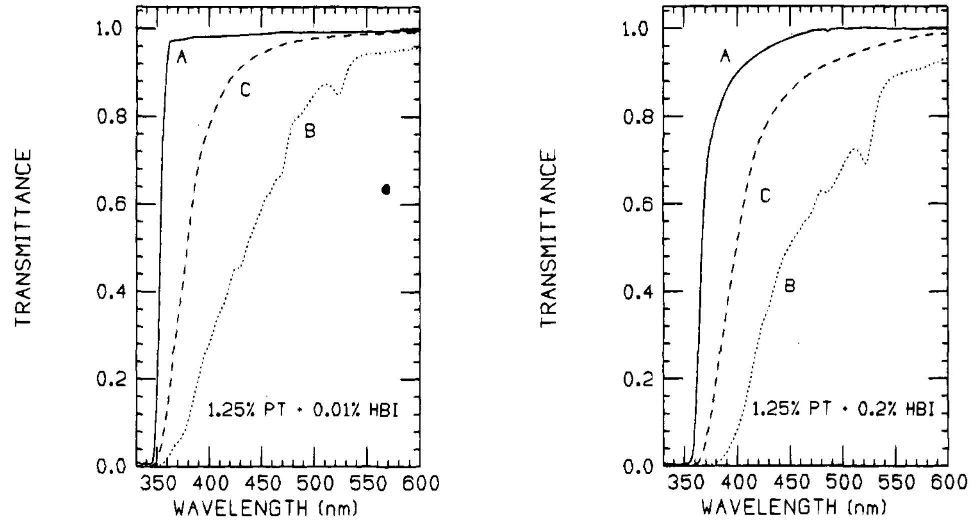

Figure 6. Irradiation of HBI-doped polystyrene samples: (A) before irradiation, (B) after 10 Mrad; (C) after oxygen annealing.

ESIPT compounds being considered for plastic scintillation applications. The light yield of the HBO derivatives is similar to that of the HBT derivatives and is too low for practical considerations, with the exception of 4PHBO. The light yield of the HBI derivatives is significantly higher than for the remaining HBT and HBO derivatives, including 3HF. The lifetimes were determined to be between 4 and 6 ns. This range is within the desirable limits, for the current goal is to develop green-emitting dopants faster than the existing ones, whose decay times are between 7 and 12 ns. For these measurements, a filter was used to remove any direct light proceeding from the primary dopant (PT). Its contribution to the measurement would give rise to an erroneously shorter decay time for the derivatives studied. The lifetime of PT is estimated to be approximately 1 ns in solution.[21]

An evaluation of the photophysical properties indicates that the HBI derivatives present an improvement in light yield while maintaining a short decay time. Their main drawback is the emission range, which is below the target region of 530−550 nm. Another dopant would need to be utilized to reach such wavelengths, or the HBI molecule would have to be modified through substitution to force a bathochromic shift. However, these HBI derivatives offer the possibility of acting as primary dopants. Because of their absorption range, given the proper concentration, they will couple directly to polystyrene and fluoresce at long wavelengths (approximately 500 nm). A primary dopant with these characteristics may be useful, since this wavelength range is only reached using a secondary dopant.

Radiation damage studies have been carried out for HBO, HBI, and their chloro-substituted derivatives. Figures 5 and 6 present the transmittance data for polystyrene samples doped with different concentrations of HBO and HBI. HBI and its derivatives presented solubility problems in styrene, and a 1% (by weight) concentration could not be attained. A concentration of 0.2% (by weight) was used. The samples were kept under a nitrogen atmosphere and exposed to γ-radiation to a total dose of 10 Mrad. The samples show a large increase in absorption immediately after irradiation. This absorption is largely transient and disappears with time. This process is accelerated by annealing the samples under an oxygen atmosphere.[4,5] As observed in other scintillators, the samples present certain permanent damage since a residual absorption remains. However,

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there are no clear signs of the formation of a new band as observed in HBT and its derivatives.

Conclusions

The HBT derivatives have short lifetimes, low quantum yield, and poor radiation resistance due to isomer formation under such conditions. The HBO derivatives present similar characteristics with the important exception of the radiation-induced isomer formation. The HBI derivatives show a good combination of decay time, light yield, and radiation resistance. However, because of their emission range they are better candidates for primary rather than for secondary dopants. In order to test them as primary dopants, their solubility in styrene needs to be improved. New HBI derivatives are being prepared to solve this problem.

Experimental Section

Instrumentation and Techniques. All melting points were determined with a Fisher-Johns apparatus and are uncorrected. Transmittance and fluorescence spectra were recorded with a Hewlett-Packard Model 8451A diode array spectrophotometer. All absorbance measurements used undoped polystyrene as the reference. The fluorescence spectra were measured using an external Hg lamp whose light was brought into the spectrophotometer by means of a quartz fiber. A band-pass filter was used to select the 334-nm excitation wavelength (03FIM026, Oriel). Front-surface (FS) excitation measurements were performed. Light from the quartz fiber excited the sample surface facing the spectrophotometer collection optics. The sample fluorescence was viewed directly. The angle of incidence with respect to the surface plane was 45° in this geometry. ^{1}H NMR spectra were determined on a Bruker WP200SY spectrometer (Me_4Si internal reference, J values given in Hz). Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer by Paulanne Ryder (Northern Illinois University, DeKalb, IL).

Emission time distributions were measured utilizing a ^{22}Na source which excited the scintillator sample being studied and a BaF_2 trigger crystal. The BaF_2 crystal was coupled to a photomultiplier (Hamamatsu assembly H3177) and provided the START signal for a LeCroy qVt operating in time mode. The geometry was such that only single photons from the plastic scintillator reached a second photomultiplier (Hamamatsu assembly H4022), which generated the STOP signal. A filter (LP400, Oriel) was positioned in front of the scintillator sample to remove light below 400 nm whose origin was nonabsorbed light from the primary dopant (*p*-terphenyl). The emission time probability distribution for these scintillators can be described by a one-exponential decay:

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

A Gaussian time error with the standard deviation σ_t was assumed. The resulting time distribution is then

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

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

Sample Preparation. Styrene monomer (50T, ARCO) was deinhibited by passage through a column filled with alumina pellets (F-200, ALCOA) and purified by vacuum distillation. Glass polymerization tubes were cleaned with nitric and sulfuric acids and treated for 10 min with a 30% solution of dichlorodimethylsilane in hexane. This treatment enabled the removal of the plastic samples once the polymerization cycle was finished. Purified styrene was poured into the polymerization tubes containing the appropriate dopants. The various solutions were degassed through repeated freeze−pump−thaw cycles. The solutions were polymerized in a silicone oil bath at 125 °C for 24 h and at 140 °C for 48 h. The bath temperature was ramped down to 90 °C over 16 h. After removal from the oil bath, the tubes were quenched in liquid nitrogen for a fast release of the polystyrene rods. The rods were cut and polished into discs of 2.2 cm diameter and 1 cm thickness.

Fluorescent Compounds. The parent compounds 2-(2′-hydroxyphenyl)benzothiazole (HBT) and 2-(2′-hydroxyphenyl)-benzoxazole (HBO) were purchased from Frinton and Aldrich, respectively, and further purified by flash chromatography. The remaining compounds were prepared using a modification of the procedure described by either Anthony *et al.*[19] (method A) or Hein *et al.*[22] (method B). All starting materials were purchased from Aldrich, with the exception of 4-phenylsalicylic acid, whose preparation followed procedures described in the literature.[23,24]

Method A. General Procedure. Equimolar amounts of 2-aminothiophenol or 2-aminophenol and the corresponding salicylic acid derivative were dissolved in dry toluene in a flask provided with magnetic stirring to form the corresponding HBT or HBO derivative, respectively. The solution was warmed to 40 °C, and an equimolar amount of phosphorus trichloride was added dropwise to the reaction mixture. The solution was heated to 100 °C for 8−12 h and then cooled to room temperature. The reaction mixture was extracted several times with a 20% (by weight) sodium carbonate solution, washed with distilled water, and then dried over magnesium sulfate. Evaporation of the solvent produced a solid residue, which was purified by flash column chromatography through silica gel.

Method B. General Procedure. Equimolar amounts of 2-aminophenol or 1,2-phenylenediamine and the corresponding salicylic acid derivative were reacted in polyphosphoric acid in a flask provided with mechanical stirring to form the corresponding HBO or HBI derivative, respectively. The solution was heated overnight at 150 °C. The reaction mixture was cooled to room temperature and poured over ice water. The precipitate formed was collected by filtration, slurried with a 10% (by weight) sodium bicarbonate solution, and filtered again. This residue was purified by flash column chromatography through silica gel.

2-(2′-Hydroxy-3′-chlorophenyl)benzothiazole (3CHBT). Reaction of 3-chlorosalicylic acid (70 mmol), 2-aminothiophenol (77 mmol), and PCl_3 (70 mmol) in toluene produced **3CHBT** in 45% yield (method A). The crude product was purified by flash chromatography through silica gel (hexane/methylene chloride, 1:1); mp 181−182 °C (lit.[19] mp 183−184 °C).

2-(2′-Hydroxy-5′-chlorophenyl)benzothiazole (5CHBT). Reaction of 5-chlorosalicylic acid (60 mmol), 2-aminothiophenol (66 mmol), and PCl_3 (60 mmol) in toluene produced **5CHBT** in 49% yield (method A). The crude product was purified by flash chromatography through silica gel (hexane/methylene chloride, 3:1); mp 150−151 °C (lit.[19] mp 149−150 °C).

2-(2′-Hydroxy-4′-methoxyphenyl)benzothiazole (4MOHBT). Reaction of 4-methoxysalicylic acid (33 mmol), 2-aminothiophenol (36 mmol), and PCl_3 (33 mmol) in toluene produced **4MOHBT** in 32% yield (method A). The crude product was purified by flash chromatography through silica gel (hexane/ethyl acetate, 4:1); mp 138−140 °C (lit.[19] mp 136−137 °C).

2-(2′-Hydroxy-3′-chlorophenyl)benzoxazole (3CHBO). Reaction of 3-chlorosalicylic acid (70 mmol), 2-aminophenol (77 mmol), and PCl_3 (70 mmol) in toluene produced **3CHBO** in 10% yield (method A). The crude product was purified by flash chromatography through silica gel (hexane/ethyl acetate, 4:1); mp 141−143 °C (lit.[25] mp 136−137 °C).

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2-(2′-Hydroxy-5′-chlorophenyl)benzoxazole (5CHBO). Reaction of 5-chlorosalicylic acid (17 mmol) and 2-aminophenol (18 mmol) in polyphosphoric acid (25 mL) produced **5CHBO** in 63% yield (method B). The crude product was purified by flash chromatography through silica gel (hexane/ethyl acetate, 4:1); mp 157−159 °C (lit.[26] mp 144 °C). Anal. Calcd for $C_{13}H_8ClNO_2$: C, 63.67; H, 3.26; N, 5.71. Found: C, 63.81; H, 3.34; N, 5.83.

2-(3′-Hydroxy-4′-biphenylyl)benzoxazole (4PHBO). Reaction of 4-phenylsalicylic acid (26 mmol) and 2-aminophenol (29 mmol) in polyphosphoric acid (80 mL) produced **4PHBO** in 43% yield (method B). The crude product was purified by flash chromatography through silica gel (hexane/ethyl acetate, 3:1); mp 170−172 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 11.55 (s, 1H), 8.1 (d, J = 8 Hz, 1H), 7.8−7.55 (m, 4H), 7.55−7.3 (m, 6H), 7.25 (d, J = 8 Hz, 1H). Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.44; H, 4.53; N, 4.88. Found: C, 79.35; H, 4.30; N, 4.96.

2-(2′-Hydroxyphenyl)benzimidazole (HBI). Reaction of salicylic acid (70 mmol) and 1,2-phenylenediamine (70 mmol) in polyphosphoric acid (100 mL) produced **HBI** in 30% yield (method B). The crude product was purified by flash chromatography through silica gel (hexane/ethyl acetate, 4:1); mp 243−245 °C (lit.[27] mp 241−242 °C).

2-(2′-Hydroxy-3′-chlorophenyl)benzimidazole (3CHBI). Reaction of 3-chlorosalicylic acid (70 mmol) and 1,2-phenylenediamine (77 mmol) in polyphosphoric acid (200 mL) produced **3CHBI** in 75% yield (method B). The crude product was purified by flash chromatography through silica gel (hexane/ethyl acetate, 1:2); mp 322−323 °C dec (lit.[25] mp 315−316 °C). Anal. Calcd for $C_{13}H_9ClN_2O$: C, 63.80; H, 3.68; N, 11.45. Found: C, 64.02; H. 3.63; N, 11.21.

2-(2′-Hydroxy-5′-chlorophenyl)benzimidazole (5CHBI). Reaction of 5-chlorosalicylic acid (70 mmol) and 1,2-phenylenediamine (70 mmol) in polyphosphoric acid (100 mL) produced **5CHBI** in 20% yield (method B). The crude product was purified by flash chromatography through silica gel (hexane/ethyl acetate, 1:2); mp 313−315 °C (lit.[27] mp 302−304 °C). Anal. Calcd for $C_{13}H_9ClN_2O$: C, 63.80; H, 3.68; N, 11.45. Found: C, 63.51; H. 3.88; N, 11.42.

2-(3′-Hydroxy-4′-biphenylyl)benzimidazole (4PHBI). Reaction of 4-phenylsalicylic acid (26 mmol) and 1,2-phenylenediamine (29 mmol) in polyphosphoric acid (75 mL) produced **4PHBI** in 63% yield (method B). The crude product was purified by flash chromatography through silica gel (cyclohexane/ethyl acetate, 3:1); mp 296−298 °C. ^{1}H NMR (200 MHz, d_6-DMSO): δ 13.25 (s, 1H), 8.15 (d, J = 8 Hz, 1H), 7.8 (d, J = 8 Hz, 1H), 7.65 (m, 2H), 7.6−7.2 (m, 8H), NH is unobserved. Anal. Calcd for $C_{19}H_{14}N_2O$: C, 79.72; H, 4.90; N, 9.79. Found: C, 79.60; H, 5.21; N, 9.54.

Irradiations. The samples for radiation damage studies were placed in stainless steel cans and evacuated for 2 weeks. The cans were then back-filled with dry nitrogen. All samples were irradiated with a ^{60}Co source at the Phoenix Memorial Laboratory of the University of Michigan at a rate of approximately 1.7 Mrad/h to a total dose of 10 Mrad. All the samples developed some coloration during the exposure, some of which disappeared with time when the samples were exposed to oxygen. For this study, the samples were kept under a 100 psig oxygen atmosphere for 8 d after their irradiation.

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