Pulse Shape Discrimination Properties of Plastic Scintillators Incorporating a Rationally Designed Highly Soluble and Polymerizable Derivative of 9,10-Diphenylanthracene

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Abstract

A highly soluble and polymerizable derivative of 9,10-diphenylanthracene was designed and synthesized specifically to be capable of achieving very high loadings (at least 50 wt.%) when copolymerized with a polyvinyltoluene (PVT) matrix. The resulting heavily crosslinked plastics are mechanically hard and robust, and were found to have exceptional clarity with no sign of dye precipitation. Samples of these plastics both with and without added wavelength shifter were characterized for light yield, scintillation decay, and pulse shape discrimination (PSD) performance for α/γ discrimination, and the results were compared to that of a commercially available PSD plastic, EJ-299-34. The best performing formulation, with a primary dye loading of 50 wt.%, had a measured light yield of 9950 photons/MeV, and achieved a PSD figure-of-merit (FOM) of 1.05, the latter indicating that while the present material is not suited for practical applications, the overall approach demonstrates a proof-of-concept of PSD in highly loaded plastics stabilized through copolymerization of the primary dye, and suggests that further improvements through better dye choice/design may yet be achievable.

Keywords: Plastic Scintillator, Pulse Shape Discrimination (PSD), 9,10-Diphenylanthracene, Polymerizable Dye

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1. Introduction

The variation in pulse shape originating from excitation from different high-energy particles is the origin of the technique of pulse shape discrimination (PSD), a technique that can be used to actively identify the type of the detected particle. In contrast to inorganic scintillators, which are among the best materials for γ -ray detection and spectroscopy, organic materials are among the most widely used materials for PSD applications [1], a primary example of which is the use of PSD based detection methods for fast-n/ γ discrimination, which is of particular interest for the detection of special nuclear material (SNM). The PSD properties of organic scintillators have a long history dating back to the 1950's [2]. Organic crystals are among the highest performing materials for n/ γ PSD, with single crystal *trans*-stilbene being readily considered as having the best known PSD performance [2, 3]. On the other hand, PSD is readily achievable in conventional liquid scintillator solutions, which have distinct advantage over organic crystals in terms of cost, scalability, and ease of manufacture and handling. There are some distinct disadvantages of organic liquids, including concerns over toxicity, flammability, the potential for leaks, and the necessity of maintaining strict oxygen free conditions of the solution throughout its life, all of which are even more problematic in the context of very large detector sizes. Despite these shortcomings, liquid scintillator solutions are among the most widely used detector materials for fast neutron spectroscopy and n/ γ discrimination.

For other types of detection, plastic scintillators offer many distinct advantages over organic or even inorganic crystals and liquid scintillator solutions, most notably low cost, very good scalability, and great ease of use and handling, with complex geometries being readily attainable due to the good machinability of typical plastic formulations. Despite all these advantages, plastic materials have until only recently long been regarded as unsuitable for PSD applications due to their inferior discrimination properties. A notable exception to this, however, is the development by Brooks et al. in 1960 of a PSD capable plastic scintillator dubbed as "Plastic 77" by the authors [4], whose commercialization was attempted under the trade name NE-150 but which was eventu-

30 ally abandoned due to issues with the material's long-term stability [5]. Only in last few
 31 years has the demonstration of commercial plastic scintillators with efficient PSD prop-
 32 erties been fully realized. The recent breakthrough was made in 2012 when Zaitseva et
 33 al. first reported the use of polyvinyltoluene (PVT) based scintillators with a high load-
 34 ing ($\geq 30\%$) of 2,5-diphenyloxazole (PPO) as the first plastic scintillator since Brooks'
 35 that was capable of achieving efficient n/γ discrimination [6]. The necessity for a high
 36 primary dye loading in plastic scintillators was hinted at in their previous work, which
 37 established the requirement in PSD capable mixed crystals of a high concentration of
 38 primary solute states in order to facilitate triplet-triplet annihilation leading to emis-
 39 sion of delayed fluorescence [7]. Since then, the material has been developed into two
 40 different commercial materials from Eljen Technology, EJ-299-33A, which has better
 41 performance but is relatively soft for a scintillating plastic, and EJ-299-34, which has
 42 better mechanical properties but decreased discrimination performance [8]. As an ex-
 43 ample of the difference in their mechanical properties, in our hands, EJ-299-33A was
 44 found to be very difficult to machine using our protocol for fabricating small disks
 45 (typically $\varnothing 10\text{mm} \times 2\text{-}5\text{mm}$) from regular sheet stock, which we developed initially
 46 for conventional plastic scintillator formulations (e.g., EJ-212). While EJ-299-34 was
 47 much more easily machined via the same process, some additional care was needed
 48 to achieve good finish prior to polishing, and some additional complications were en-
 49 countered when attempting to affix the samples for polishing with low melting point
 50 adhesives ($T_M \sim 55^\circ\text{C}$, actual working temp. $\sim 60\text{-}80^\circ\text{C}$), namely some deformation
 51 and surface hazing. While alternative and more optimized machining techniques quite
 52 probably can achieve good results with either material, it would be advantageous to
 53 have a PSD capable plastic that in general has as good if not better machinability than
 54 traditional scintillating plastic formulations so that costs associated with the processing
 55 of the material can be minimized. The mechanical properties of the all these materials
 56 are directly related to the high dye loading that enables them to be efficient at pulse
 57 shape discrimination. With such high loadings, the dye molecules act as effective plas-
 58 ticizing agents, rendering the resulting material softer than either the base plastic alone
 59 or conventional plastic scintillator formulations. Martinez et al. have shown that sub-
 60 stitution of of the aromatic polymer matrices with a non-aromatic material such as

61 poly(methyl methacrylate) (PMMA) can be advantageous due to its higher hardness,
62 but the discrimination performance was again diminished [9].

63 Another potential problem arising from the use of high primary dye loading is the
64 long term stability of the material, which is a principal issue needing to be addressed
65 with regards to the current generation of PSD capable plastics. The failure of Brook's
66 "Plastic 77" to be fully realized as the NE-150 commercial material was largely due
67 to the dramatic loss of transparency and whitening which took place over time [5],
68 presumably due to precipitation of the highly loaded dye components. Blanc et al.
69 have experimented further with the Plastic 77 composition and demonstrated that both
70 incorporating polymerizable additives and cross-linking of the polymer matrix were
71 effective means of preventing precipitation of the dye components [10]. In general,
72 with no other means of fundamentally preventing dye crystallization, a high dye load-
73 ing will quite likely lead to precipitation, either during fabrication or upon aging, since
74 it will be quite likely that the dye will be above its solubility limit in the cured plastic.
75 The reason for this is at the elevated polymerization temperature with which plastics
76 are typically cured, the dye will typically have a significantly higher solubility than in
77 the monomer at room temperature. If a plastic is cured with a dye content at or near
78 the high temperature solubility limit, upon cooling to room temperature there will be a
79 significant degree of supersaturation of the dye, which can lead to precipitation either
80 during the cooling itself, leading to an opaque material, or slowly over time, leading to
81 a gradual loss of transparency. Additionally, the thermodynamic solubility limit of the
82 dye in a polymer may be fundamentally lower than in the liquid monomer at any given
83 temperature, which again would lead to a situation of supersaturation of the dye in
84 the cured plastic. Lower dye loadings can be utilized to improve long term stability of
85 the material, but not without some sacrifice in PSD performance (at least for presently
86 known PSD-capable dyes). As such, development of new approaches to stabilization
87 of high dye loadings remains a key objective for the development of new PSD capable
88 plastics.

89 In this work, we address several key factors to the design of novel primary dyes to
90 specifically address all of the issues associated with the high dye loading method. First
91 and foremost is the need for a primary dye with high solubility to achieve loadings

92 capable of effecting good PSD performance, but without leading to precipitation of the
93 dye or loss of mechanical properties, especially at timescales corresponding to the ex-
94 pected useful lifetime of the material. While PPO has been shown to be a PSD capable
95 dye in plastic scintillators, it is anticipated that there are a number of other possible can-
96 didates, some of which may be able to achieve significantly better performance than
97 even the best commercial PSD plastic. However, there are very few if any efficient
98 and common scintillating dyes other than PPO or its derivatives that have solubilities
99 in aromatic solvents high enough to achieve decent PSD performance [6, 11]. With
100 all this in mind, our main approach was to identify a candidate scintillating dye with
101 overall good properties and good PSD performance, and then functionally derivatize
102 the parent molecule to overcome the shortcoming of solubility and stability in the final
103 plastic. To achieve the former, the introduction of long, flexible, and/or branched alkyl
104 chains can greatly enhance solubility while simultaneously lowering the compounds
105 melting point, while for the latter, the introduction of polymerizable groups can allow
106 for direct bonding of the dye to the polymer backbone, eliminating the ability of the
107 dye to precipitate from the plastic upon cooling. It is worth noting that at least one
108 previous attempt has been made, albeit unsuccessfully, to directly incorporate a scintil-
109 lating dye via copolymerization into a PSD-capable plastic. In their report, O'Bryan et
110 al. demonstrated PMMA-based plastic scintillators loaded up to 30 wt.% with a poly-
111 merizable *trans*-stilbene derivative, but the resulting material failed to demonstrate any
112 performance for n/γ PSD [12].

113 With all of these factors in mind, we set out to synthesize an entirely new primary
114 dye that was rationally designed to fulfill each of these key requirements. Our specific
115 approach reported herein is based upon the derivatization of 9,10-diphenylanthracene
116 (DPA), a scintillating dye known in single crystal form to possess both good PSD and
117 overall scintillator performance [13–15], and fig. 1 details the chemical structure of our
118 proposed primary dye (DPA-DHS, where DHS='dihexylstyrene'). Functionalization
119 of the DPA core by introduction of aryl ether linkages onto the pendant phenyl rings
120 introduces the flexible hexyl spacer groups, whose primary intended function is to en-
121 hance the solubility of the dye while simultaneously lowering its melting point, both
122 of which are critical factors in allowing for the required high loading content. At the

Figure 1: Structure of the DPA-DHS dye monomer (numbering of the anthracene core shown for reference).

distal end of the spacer chains are styrenyl groups, which are purposefully included in our proposed structure over other potential polymerizable groups in an attempt to achieve optimal incorporation of the dye into the overall polymer matrix. In addition, the presence of two polymerizable groups per dye molecule was intended to allow the dye to simultaneously act as a cross-linker for the matrix, and since high loadings are sought after, such a high degree of cross-linking would lead to a material that is quite hard and tough, potentially more so than the current generation of PSD plastics.

2. Experimental

2.1. General Remarks

All starting materials for synthetic procedures were purchased from commercial sources and used as received. Anhydrous THF was obtained via distillation over Na/benzophenone. Anhydrous DCM and DMF were purchased predried over molecular sieves. ^1H and ^{13}C NMR spectra were obtained using either a Bruker DRX500 spectrometer using a 5 mm broadband probe or a Bruker AV500 spectrometer with a 5 mm cryoprobe. Melting points were obtained using a microscope fitted with an Instec HC621V-F8 hot stage and mK1000 temperature controller.

2.2. Overall Synthesis of the DPA-DHS Monomer

The synthetic scheme for the synthesis of the DPA-DHS monomer is shown in fig. 2. There are five discrete steps in total with a four-step sequence being the longest

linear branch with an overall yield of 55%. The synthesis includes as one of its intermediates the dimethoxy-functionalized DMPA, which was additionally utilized as a model compound to investigate the impacts to the photoluminescence properties of DPA-DHS by the introduction of the polymerizable side chains.

Figure 2: Synthetic Scheme for the synthesis of DPA-DHS.

2.2.1. Synthesis of 9,10-Bis(4-methoxyphenyl)anthracene-9,10-diol (2)

To a solution of 3.76 mL (30.0 mmol; 2.5 eq.) of 4-bromoanisole (1) in 60 mL of dry THF at -78 °C under Ar was dropwise added 12.0 mL (30.0 mmol; 2.5 eq.) of 2.5 M n-butyllithium in hexanes. After stirring at -78 °C for 1 hour, the solution was transferred dropwise via cannula to a suspension of 2.50 g (12.0 mmol; 1 eq.) of anthraquinone in 50 mL of dry THF at -78 °C. The resulting solution was warmed to room temperature and stirred for 18.5 hours, then cooled to 0 °C and quenched with 20 mL of sat. NH_4Cl . The reaction contents were poured into 250 mL of H_2O , and the resulting mixture was extracted with 3×125 mL of Et_2O . The combined organic layers were washed with 2×250 mL of sat. NaCl and dried over MgSO_4 . After removal of the solvent under vacuum, the crude product was preadsorbed onto silica gel before flash

157 chromatography with 3:1 Hexane:EtOAc followed by 1:1 Hexane:EtOAc to give 4.69
158 g (92.0% yield) of **(2)**.

159 $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ = 7.78-7.73 (m, 4H), 7.40-7.35 (m, 4H), 6.81-6.77 (m,
160 4H), 6.46-6.42 (m, 4H), 3.64 (s, 6H), 2.97 (s, 2H).

161 $^{13}\text{C-NMR}$ (500 MHz, CDCl_3) δ = 158.28, 141.27, 136.83, 128.69, 127.91, 126.71,
162 112.93, 74.67, 55.20.

163 2.2.2. *Synthesis of 9,10-Bis(4-methoxyphenyl)-anthracene (DMPA)*

164 To a room temperature solution of 2.96 g (6.97 mmol; 1 eq.) of **(2)** in 75 mL
165 of THF that was sparged with Ar for 15 minutes was added a solution of 15.73 g
166 (69.7 mmol; 10 eq.) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 60 mL of 10% (wt/v) HCl. The reaction was
167 sparged with Ar for an additional 10 minutes, and after stirring at room temperature for
168 4.75 hours, the contents were diluted with 75 mL of H_2O and filtered. The collected
169 product was washed with H_2O and MeOH, dried under vacuum, and recrystallized
170 from CHCl_3 /cyclohexane to give 2.46 g (90.4% yield) of **(DMPA)**.

171 $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ = 7.76-7.71 (m, 4H), 7.42-7.37 (m, 4H), 7.35-7.31 (m,
172 4H), 7.17-7.12 (m, 4H), 4.00-3.94 (s, 6H).

173 $^{13}\text{C-NMR}$ (500 MHz, CDCl_3) δ = 159.15, 136.89, 132.53, 131.29, 130.40, 127.18,
174 125.03, 114.00, 55.55.

175 2.2.3. *Synthesis of 9,10-Bis(4-hydroxyphenyl)-anthracene (3)*

176 To a suspension of 3.11 g (7.96 mmol; 1 eq.) of **(DMPA)** in 150 mL of dry DCM at
177 0 °C under Ar was dropwise added 17.5 mL (17.5 mmol; 2.2 eq.) of 1M BBr_3 in DCM.
178 The reaction was slowly warmed to room temperature and stirred for 16 hours, then
179 cooled again to 0 °C before quenching with 30 mL of 10% (wt/v) HCl. The resulting
180 mixture was warmed to room temperature, poured into 150 mL of H_2O , and extracted
181 with 3×175 mL of EtOAc. The combined organic layers were washed with 300 mL
182 of H_2O , 300 mL of sat. NaHCO_3 , and 300 mL of sat. NaCl, then dried over MgSO_4 .
183 After removal of the solvent under vacuum, the crude product was preadsorbed onto

184 silica gel before flash chromatography with 2:1 Hexane:EtOAc to give 2.61 g (90.7%
185 yield) of (**3**).

186 ¹H-NMR (500 MHz, THF-*d*₈) δ = 8.51 (s, 2H), 7.75-7.70 (m, 4H), 7.29-7.25 (m, 4H),
187 7.24-7.20 (m, 4H), 7.00-6.97 (m, 4H).

188 ¹³C-NMR (500 MHz, THF-*d*₈) δ = 158.25, 137.89, 133.06, 131.34, 130.46, 127.84,
189 125.38, 116.08.

190 2.2.4. Synthesis of 6-[(4-Ethenylphenyl)methoxy]-1-hexanol (**5**)

191 To a suspension of 2.00 g (50.0 mmol; 1 eq.) of 60% NaH in 100 mL of dry DMF
192 at 0 °C under Ar was carefully added 17.73 g (150.0 mmol; 3 eq.) of 1,6-hexanediol
193 (**4**) against a counterflow of Ar. The mixture was warmed to room temperature and
194 stirred for 1 hour, then cooled to 0 °C before dropwise adding 7.75 mL (55.0 mmol;
195 1.1 eq.) of 4-vinylbenzyl chloride. The reaction was warmed to room temperature and
196 stirred for 17.5 hours, then poured into 500 mL of H₂O and extracted with 3 $\times$ 200
197 mL of Et₂O. The combined organic layers were washed with 2 $\times$ 400 mL of H₂O
198 and 400 mL of sat. NaCl, then dried over MgSO₄. After removal of the solvent under
199 vacuum, the crude product was purified via flash chromatography on silica gel with 3:1
200 Hexane:EtOAc to give 8.72 g (74.4% yield) of (**5**).

201 ¹H-NMR (500 MHz, CDCl₃) δ = 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz,
202 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.23 (dd,
203 *J* = 10.9, 0.9 Hz, 1H), 4.48 (s, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 3.46 (t, *J* = 6.6 Hz, 2H),
204 1.82 (s, 1H), 1.62 (quin, *J* = 6.9 Hz, 2H), 1.56 (t, *J* = 6.9 Hz, 2H), 1.43-1.32 (m, 4H).

205 ¹³C-NMR (500 MHz, CDCl₃) δ = 138.29, 136.95, 136.64, 127.92, 126.28, 113.77,
206 72.66, 70.37, 62.86, 32.74, 29.77, 26.07, 25.66.

207 2.2.5. Synthesis of 9,10-Bis[4-({6-[(4-ethenylphenyl)methoxy]hexyl}oxy)phenyl]anthra- 208 cene (**DPA-DHS**)

209 To a solution of 1.33 g (3.67 mmol; 1 eq.) of (**3**), 2.58 g (11.0 mmol; 3 eq.) of (**5**),
210 and 1.73 mL (11.0 mmol; 3 eq.) of diethylazodicarboxylate in 70 mL of dry THF at

0 °C under Ar was dropwise added a solution of 2.89 g (11.0 mmol; 3 eq.) of triphenylphosphine in 25 mL of dry THF with the formation of a precipitate. The reaction was warmed to room temperature and stirred for 24 hours, after which all of the precipitate had redissolved. The reaction solvent was removed under vacuum, and the crude mixture was purified via flash chromatography on silica gel with 1:3 Hexane:DCM to give 2.39 g (81.9% yield) of (**DPA-DHS**) as a pale yellow solid (m.p. 119-123 °C).

¹H-NMR (500 MHz, CDCl₃) δ = 7.78-7.73 (m, 4H), 7.42-7.40 (m, 4H), 7.39-7.36 (m, 4H), 7.36-7.31 (m, 8H), 7.15-7.11 (m, 4H), 6.72 (dd, J = 17.6, 10.9 Hz, 2H), 5.75 (dd, J = 17.6, 0.9 Hz, 2H), 5.23 (dd, J = 10.9, 0.9 Hz, 2H), 4.52 (s, 4H), 4.11 (t, J = 6.5 Hz, 4H), 3.52 (t, J = 6.5 Hz, 4H), 1.91 (quin, J = 6.9 Hz, 4H), 1.72 (quin, J = 6.9 Hz, 4H), 1.63-1.49 (m, 8H).

¹³C-NMR (500 MHz, CDCl₃) δ = 158.45, 138.20, 136.80, 136.70, 136.48, 132.26, 130.85, 130.17, 127.76, 126.96, 126.14, 124.74, 114.28, 113.61, 72.55, 70.21, 67.88, 29.67, 29.28, 25.99, 25.95.

2.3. Scintillator Sample Fabrication

Coumarin 6 (Sigma-Aldrich) and 1,1-di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane (initiator; Acros) were used as received. Methystyrene (60% meta, 40% para, & 1% ortho mixture of isomers; Sigma-Aldrich) was degassed via freeze-pump-thaw and passed through a short column of inhibitor remover (Sigma-Aldrich) prior to use. Glass shell vials with internal diameters of 10 mm were cleaned in piranha solution immediately before vapor treatment under house vacuum with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (Gelest). All samples were prepared by mixing each component along with 0.5 wt.% of initiator and heating at 80 °C for 24 hours under N₂. After cooling to room temperature, the vials were broken to remove the cured samples, which were further ground and polished to the desired thickness.

2.4. Characterization Methods

Absorbance spectra of solutions were acquired using a Shimadzu UV-1700 UV-Visible Spectrophotometer and were referenced again a solvent blank. Photoluminescence spectra were acquired using a QuantaMaster QM-4/SE (Photon Technology

Inc.) fluorometer. Emission spectra for solutions were acquired using 10mm quartz cells in the standard right-angle geometry, while spectra for plastic samples were acquired using a right angle geometry specially offset to avoid collection of light emitted directly from the sample surface, in order to best represent the technical emission spectrum of the scintillator samples as viewed by a PMT during actual detection tests. Photoluminescence quantum yields (ϕ_{PL}) of solutions were measured via the absorbance and fluorescence spectra of a series of concentrations for degassed (freeze-pump-thaw) samples using DPA in cyclohexane ($\phi_{PL} = 1$) [16] as the reference standard, and the concentration of all solutions were kept sufficiently low as to achieve absorbances no greater than 0.1 AU over the range of concentrations.

Gamma-ray spectra under ^{137}Cs irradiation were recorded using a Canberra Lynx Digital Signal Processor; a custom machined PTFE sample holder was used to ensure placement accuracy and optical grease was used to couple the sample to the window of a Hamamatsu R878 PMT, which itself was plugged into a Canberra Model 2007P Photomultiplier Tube Base/Preamplifier. All spectra were recorded using a trapezoidal shaping filter with a 1.0 μs rise time and a 0.5 μs flat-top time. The relative Compton edge positions were compared to identically sized specimens of EJ-212 (Eljen Technology, Inc.) that were machined and polished from larger pieces of sheet stock. The acquired photoluminescence data was used along with the quantum efficiency curve for the PMT photocathode to correct the relative Compton edge positions for the emission spectrum of each sample. In this manner, absolute light yields were obtained from the manufacturer's specification for the light yield of EJ-212 (10,000 photons/MeV).

Time resolved radioluminescence decay curves were measured using a time-correlated single photon counting (TCSPC) based approach utilizing a Hamamatsu H2431-50 assembly as the start PMT and a Hamamatsu H10721P-110 module fitted with an E5776-51 SMA fiber optic adapter as the stop PMT. A bare terminated 800 μm multi-mode fiber was used along with a custom machined PTFE sample holder to allow the stop PMT to collect single photons from the sample; under ^{137}Cs irradiation, the sample was directly coupled using optical grease to the window of the start PMT, but under ^{210}Po irradiation, the PTFE sample holder and source were placed inside a specially constructed vacuum chamber with a quartz disk end-window, onto which the

271 start PMT was coupled. The signal from the stop PMT was fed into a Ortec Model
272 9326 Fast Preamplifier, and the resulting output along with the signal from the start
273 PMT was digitized using a PicoScope Model 5244B Oscilloscope (Pico Technology,
274 Inc.) operated in 8-bit mode with a digitization rate of 500 MS/sec. The differences
275 in arrival times between single photon pulses detected by the stop PMT and the main
276 pulse detected by the start PMT were histogrammed to obtain the scintillation decay
277 curves over a 2 μ s interval.

278 Pulse-shape discrimination tests were performed under simultaneous α/γ irradiation,
279 which was done in lieu of the more commonplace n/γ PSD testing on account
280 of the fact that NRC exempt quantities of both γ and α (specifically ^{210}Po) emitters
281 are readily available, inexpensive, and can be purchased and handled without special
282 precautions or license (no such NRC exempt quantity is currently available for neutron
283 emitting sources). Pulses from samples under irradiation were acquired using a Hamamatsu
284 R6321-100 PMT that was coupled to the quartz disk end-window of a specially
285 constructed vacuum chamber. The sample under test was coupled to the vacuum side of
286 the end-window using optical grease, and was held in place using a custom machined
287 PTFE sample holder, which also held in place the mixed source assembled from separate
288 ^{210}Po and ^{137}Cs sources. Raw pulses obtained from the PMT anode were digitized
289 using the Picoscope Model 5244B Oscilloscope operated in 12-bit mode with a digitization
290 rate of 500 MS/sec and were saved directly to disk for off-line analysis. Energy
291 calibration of the resulting data sets was performed by histogramming the total integral
292 of each pulse and finding the position of the Compton edge of the gamma distribution.
293 Two-dimensional plots representing the PSD performance were obtained using a digital
294 charge comparison method to give a plot of $(Q_{\text{tail}}/Q_{\text{total}})$ versus equivalent particle
295 energy (keV-ee) [17–21].

296 3. Results & Discussion

297 3.1. Spectral and Electronic Properties of the DPA-DHS Monomer

298 The absorbance and photoluminescence spectra of DPA, DPA-DHS, and the intermediate
299 compound DMPA, are shown in fig. 3 and fig. 4, respectively. In these

Figure 3: Absorbance spectra of DPA, DPA-DHS, and DMPA as dilute solutions in CHCl_3 .

spectra, the effects that the introduction of the ether linkage to the DPA core have on the electronic structure of DMPA and DPA-DHS can readily be observed. In fig. 3, a very slight red shifting (~ 2 nm) of the absorbance maxima of DMPA and DPA-DHS is observed relative to DPA, and there is additional broadening of the vibronic sublevels for the former compounds. In fig. 4, the redshifting of the DMPA and DPA-DHS emission spectra relative to DPA is more prominent (~ 10 nm), and again broadening of the vibronic sublevels is observable. Given that the value of the redshifting is much smaller for the absorbance spectrum, it is reasonable to conclude that the main effect of the introduction of the alkoxy substituents onto the electronic properties of DMPA and DPA-DHS is to introduce additional stabilization to their respective S_1 states relative to that of DPA, while leaving the transition energies at the corresponding ground state geometries relatively unchanged from one another. Additionally, the extra degrees of freedom to the vibrational modes introduced via the alkoxy substituents is a likely factor controlling the increased broadening of the vibronic sublevels of the spectra of DMPA and DPA-DHS. Overall, DMPA and DPA-DHS have virtually identical spectra to one another, which is indicative that increasing the length of the alkyl chain

Figure 4: Photoluminescence Spectra of DPA, DPA-DHS, and DMPA as dilute solutions in toluene.

attached to the aryl ether linkage has little if any effect on the electronic properties of the DPA core. The photoluminescence quantum yields (ϕ_{PL}) of DMPA and DPA-DHS in toluene were measured to be 0.84 and 0.95, respectively. The value of ϕ_{PL} measured for DMPA is noticeably higher than a previously reported value of 0.59 [22], although the authors do not specify whether the measurements were performed on deoxygenated solutions, which could account for the observed discrepancy. Overall, the modification of the DPA core to obtain the final structure of DPA-DHS, especially given the latter's high ϕ_{PL} , does not appear to significantly disrupt its potential performance as a scintillating dye, at least in terms of its molecular emission.

3.2. Fabrication & Photoluminescence of DPA-DHS/PVT Samples

The DPA-DHS monomer obtained from our synthetic efforts was found to be quite amenable to processing through standard solution casting methods. A large reduction in melting point on account of the structural modifications was observed for DPA-DHS (~ 120 °C) as compared to 9,10-diphenylanthracene (~ 250 °C). While loadings of ≤ 10 wt.% could dissolve in methylstyrene at room temperature, heating the undissolved mixture to the curing temperature of 80 °C along with gentle agitation was able to

332 achieve full dissolution of loadings as high at 50 wt.%. Higher loading may even be
333 possible but become very difficult to achieve practically; as the DPA-DHS content is
334 increased, the dye/monomer solution becomes very viscous, and with the high degree
335 of cross-linking, the solution begins to rapidly gel within a few minutes, after which
336 further mixing becomes impossible. The rapid gelation of the DPA-DHS/PVT samples
337 (due to the cross-linking nature of its multiple polymerizable end-groups) is in direct
338 contrast to DPA/PVT samples with DPA content ranging from 0.5-2.5 wt.% fabricated
339 for comparative purposes, for which noticeable gelation was observable only after a
340 few hours into the curing.

341 The obtained plastic scintillator samples were found to good clarity, with no signs
342 of phase separation, cloudiness, or precipitation of the primary dye. As a qualitative
343 assessment of the outcome of the copolymerization, samples of DPA-DHS/PVT along
344 with cast PVT obtained through the same polymerization procedure but with no added
345 dye were subjected to swell tests in DCM. After several hours, which was an adequate
346 amount of time to achieve full dissolution of the cast PVT, the DPA-DHS/PVT sam-
347 ples showed varying degrees of swelling, with the lowest loading of DPA-DHS tested
348 (3 wt.%) showing a significant volume expansion, and the highest loading (50 wt.%)
349 demonstrating only minimal volume expansion). Thus, the degree of crosslinking (i.e.,
350 resistance to swelling) is directly dependent on the loading of the DPA-DHS, which is a
351 direct indicator of incorporation of the crosslinking DPA-DHS monomer into the poly-
352 mer matrix (which is otherwise non-crosslinking). Additionally, some residual amount
353 of unreacted or oligomeric DPA-DHS monomer was evidenced via the fluorescence of
354 the swelling solution at the end of the tests, which is not unexpected given that residual
355 monomer is commonly observed for the bulk polymerization of plastics [23, 24]. All
356 of the DPA-DHS containing samples prepared were found to be mechanically robust
357 and easily polished, as is to be expected from their crosslinking. DPA-DHS/PVT sam-
358 ples with no added wavelength shifter ranged from nearly colorless at low DPA-DHS
359 content to a pale yellow in color at the highest DPA-DHS concentrations.

360 Additional DPA-DHS/PVT samples were prepared with 0.05 wt.% of Coumarin 6
361 added to act as a wavelength shifter; Coumarin 6 was chosen for this role on account
362 of the good matching of its absorbance spectrum to the molecular emission spectrum

of DPA-DHS, which is illustrated in fig. 5. Wavelength shifters employed in most

Figure 5: Emission/Absorbance spectra of Coumarin 6, overlaid with the emission spectrum of DPA-DHS, all as dilute solutions in toluene.

363

364 commercial plastics (e.g., 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP)) are typi-
 365 cally blue to violet emitters themselves, and their absorbance spectrums do not match
 366 well with the emission spectrum of DPA-DHS. In addition, the Stokes-shift for a wave-
 367 length shifter can not be excessively small (i.e., in an attempt to shorten the emission
 368 wavelength), as this would cause too much overlap of the shifters absorption/emission
 369 spectra, and would lead to excessive self absorption by the shifting dye, defeating its
 370 intended purpose. As such, the use of a green emitting wavelength shifter such as
 371 Coumarin 6 is necessary for the DPA-DHS/PVT system to maximize the number of
 372 out-coupled photons, although the primary consequence will be that the longer wave-
 373 length photons will have a lower detection efficiency by typical blue-sensitive PMTs
 374 (which in our measurements is factored out through spectral sensitivity correction as is
 375 described in section 2.4). Samples wavelength shifted with 0.05 wt.% of Coumarin 6
 376 were bright yellow-green in color, and representative photographs of the unshifted and
 377 shifted DPA-DHS samples along with EJ-299-34 for comparison are shown in fig. 6.

The emission spectra of the commercial EJ-299-34, unshifted 50 wt.% DPA-DHS/PVT,

Figure 6: Photographs of (left) EJ-299-34, (middle) unshifted 50 wt.% DPA-DHS/PVT, and (right) Coumarin-6 shifted 50 wt.% DPA-DHS/PVT.

378

379 and Coumarin 6 shifted 50 wt.% DPA-DHS/PVT plastic scintillator samples is shown
 380 in fig. 7, along with a plot of the photo detection efficiency of a typical blue sensitive
 PMT photocathode (Hamamatsu R878). The emission for the unshifted samples was

Figure 7: Emission Spectra of EJ-299-34, unshifted 50 wt.% DPA-DHS/PVT, and Coumarin 6 shifted 50 wt.% DPA-DHS/PVT.

381

382 bright blue in color, with emission maxima centered around 450 nm. This is slightly
 383 longer in wavelength than the commercial EJ-299-34 plastic, with an emission max-
 384 imum centered at 425 nm. Samples wavelength shifted with Coumarin 6 displayed

385 bright green emissions with their maxima around 510 nm.

386 3.3. γ Light Yields of DPA-DHS/PVT Samples

387 Figure 8 plots the measured ^{137}Cs light yields as a function of DPA-DHS content
388 for DPA-DHS/PVT samples with both no added wavelength shifter, and shifted with
0.05 wt.% of Coumarin-6. Additionally, fig. 8 also plot the light yields for a series of

Figure 8: Light yields of unshifted DPA-DHS/PVT samples (top & bottom axis), Coumarin 6 shifted DPA-DHS/PVT samples (top & bottom axis), and unshifted DPA/PVT reference samples (bottom axis only).

389 comparative DPA/PVT samples with no added wavelength shifter, and prepared with
390 DPA concentrations ranging from 0.5 to 2.5 wt.%, which serve as an additional means
391 of comparing the scintillation properties of the DPA-DHS monomer to that of unfunc-
392 tionalized DPA. When the primary dye contents are compared on a concentration basis,
393 it can clearly be seen that at least in the measurable range (for DPA) of lower dye load-
394 ing, the light yields of the unshifted DPA/PVT and unshifted DPA-DHS/PVT are nearly
395 identical to one another, with the DPA/PVT slightly outperforming the DPA-DHS/PVT
396 samples. This slightly higher performance is in all likely hood directly attributable to
397

the slightly higher ϕ_{PL} of DPA compared to DPA-DHS. The close correspondance of the light yields of DPA/PVT and DPA-DHS/PVT is a strong indicator that, at least in the lower concentration range, the scintillating properties of the two primary dyes are functionally equivalent to one another, and that copolymerization with the PVT matrix does not lead to quenching of the DPA-DHS dye. For both shifted and unshifted DPA-DHS/PVT, the samples with a loading of 20 wt.% split the plots into two distinct regions. Below 20 wt.%, the light yield in the unshifted samples is strongly rising up to a maximum of 8200 photons/MeV at 5 wt.%, and then again falling down to a local minimum of 7300 photons/MeV at 20 wt.%. A similar behavior is also seen in the data for the shifted samples, although the light yield at 5 wt.% loading is a slightly higher 8600 photons/MeV but falls much more slowly to a minimum of only 8350. Above 20 wt.%, the light yields of the unshifted samples remain largely unchanged, except for a slight positive trend up to 7600 photons/MeV at 50 wt.% loading, but for the shifted samples, a strong positive trend is evident up to 9950 photons/MeV, which is the highest for any of the samples DPA-DHS samples tested.

It is well known that DPA is relatively immune to the effects of concentration quenching, due to steric interaction of the phenyl rings at the 9,10-positions preventing the formation of excimer excited states [13, 25–28]. In addition, the γ light yield for high quality single crystal DPA has been reported by van Loef et al. as 16,000 photons/MeV [15]. If one assumes that these basic properties are approximately the same for the DPA cores in the DPA-DHS plastic, then the trends observed in our light yield data can be explained as follows. At a DPA-DHS content around 5 wt.%, the concentration is high enough to ensure efficient transfer of excitation energy from the PVT matrix (although this efficiency is quite likely less than unity), and yet the concentration is still low enough that effects of self absorption by DPA-DHS are still low enough that the overall light yield is maximized in this region. As the DPA-DHS content is increased up to 20 wt.%, the efficiency of energy transfer from host to dye is relatively unchanged, but the increasing concentration of DPA-DHS is leading to a greater contribution of self absorption by DPA-DHS. For the unshifted samples, with no means of preventing loss due to self absorption, the light yield is falling in this region much faster than for the shifted ones. Above 20 wt.%, the same effects of an ever increas-

ing contribution of DPA-DHS self absorption is still present, but at concentrations this
 high, it is no longer a valid assumption that primary excitation is occurring only on the
 PVT host, since at this point a significant volume fraction of the material is occupied by
 the DPA cores. Direct excitation of the cores by the passage of the high energy particle
 is expected to be a more efficient luminescent process, since no transfer of excitation
 energy needs to take place, and thus the luminescent efficiency for direct excitation de-
 pends only on the quantum yield of the dye. As the DPA-DHS content is increased up
 to 50 wt.%, a greater proportion of excitation is occurring directly on the DPA cores,
 and thus the overall scintillation efficiency (before factoring in the effects of self ab-
 sorption) is increasing. For the unshifted samples, the increasing efficiency and the
 increasing effect of self absorption are directly competing to keep the light yield rela-
 tively unchanged, whereas for the shifted samples, the strong effect of the increasing
 efficiency is directly observable.

3.4. γ - and α -Scintillation Decays of EJ-299-34 and DPA-DHS/PVT Samples

Figure 9 compares the peak-normalized scintillation decay of the EJ-299-34 com-
 mercial plastic under both α - and γ -irradiation, while fig. 10 plots the corresponding
 data for both unshifted and Coumarin 6 shifted DPA-DHS samples at loadings of both
 10 wt.% and 50 wt.% of primary dye. The decay curves obtained for EJ-299-34 typify
 the behavior expected for a material with good PSD performance, as there is a sub-
 stantial increase in the fraction of light emitted as part of the decayed component upon
 going from γ - to α -excitation. While the decay curves of the unshifted and Coumarin
 6 shifted 50 wt.% DPA-DHS samples (fig. 10(b) and fig. 10(d)) do show increases in
 the delayed light component upon α -excitation, the relative changes are noticeably less
 than that observed for EJ-299-34. The relative change in the fraction of delayed light
 is higher for the Coumarin 6 shifted sample as compared to the unshifted one. From
 the α -decay data, it can be observed that at a time of 1 μ s, the emission for all three
 of these samples has decayed to approximately the same value, nominally 0.1% of
 the peak value. However, the main difference in these samples lies in the proportion
 of delayed emission in the decay curves under γ -excitation. At 500 ns, the emission
 from EJ-299-34 has decayed to $\sim 0.05\%$ of the peak value, while at 1 μ s, the emis-

Figure 9: Scintillation Decay of EJ-299-34 under α - & γ -irradiation.

459 sion has decayed to just above 0.01%. For both the shifted and unshifted 50 wt.%
 460 DPA-DHS samples, the emission at these time points is noticeably higher, and for the
 461 unshifted sample in particular the emission at 500 ns has decayed to just under 0.1%
 462 of the peak value, and to $\sim 0.02\%$ at 1 μs . This greater proportion of delayed emission
 463 under γ -excitation is the primary factor that is causing the decreased change in delayed
 464 emission observed for these samples. The decay curves of the unshifted and Coumarin
 465 6 shifted 10 wt.% DPA-DHS samples (fig. 10(a) and fig. 10(c), respectively) have sig-
 466 nificantly lower proportions of delayed light as compared to EJ-299-34 or the 50 wt.%
 467 DPA-DHS samples. For instance, at a time of 1 μs , the emission under α -excitation for
 468 both of these samples has decayed to a value just above 0.01% of the peak value. This
 469 is to be expected, since the primary dye content at this loading level is inadequate to
 470 allow for efficient triplet migration and subsequent annihilation. Furthermore, there is
 471 little difference in either sample between the fraction of delayed light between γ - and
 472 α -excitation.

473 The scintillation decay data also serves to provide additional evidence for the role
 474 that self-absorption plays in the difference in performance between the unshifted and

Figure 10: Comparison of Scintillation Decays of DPA-DHS/PVT Samples.

475 Coumarin 6 shifted DPA-DHS/PVT samples. Table 1 summarizes the values of the fast
 476 scintillation decay components of the tested samples that were obtained from fits of the
 477 lifetime data. From these values, it can clearly be seen that significantly longer prompt
 478 decay times were observed for both the 10 wt.% and 50 wt.% loadings of the unshifted
 479 samples (~ 10 ns) as compared to the shifted (~ 5 ns), despite the equivalent DPA-DHS
 480 content between the two groups. It is known that the observed lifetimes of organic
 481 scintillators depend both on the thickness and degree of self absorption with the mate-
 482 rial, since fluorescence photons absorbed by the sample may still be re-emitted, but the
 483 timing of this secondary emission is still governed by the molecular fluorescence decay
 484 lifetime [29]. Given this fact, it can be clearly seen that this increase in prompt decay
 485 time for the unshifted samples is directly attributable to their higher degree of self ab-
 486 sorption. A further example of this can be seen in the Coumarin 6 shifted samples,
 487 where the 50 wt.% sample was found to have slightly longer prompt decay times than
 488 the 10 wt.% sample, which would suggest that at the highest DPA-DHS concentrations,

Sample	DPA-DHS Content	Source	Fast Decay (ns)
EJ-299-34	–	^{137}Cs	3.3
		^{210}Po	3.5
Unshifted	10 wt. %	^{137}Cs	9.9
DPA-DHS		^{210}Po	10.1
	50 wt. %	^{137}Cs	9.6
		^{210}Po	10.5
Coumarin 6	10 wt. %	^{137}Cs	4.7
Shifted		^{210}Po	5.0
DPA-DHS	50 wt. %	^{137}Cs	5.4
		^{210}Po	6.2

Table 1: Fast Scintillation Decay Components of Tested Samples.

the self absorption begins to directly compete with the much more efficient absorption by the wavelength shifting dye.

3.5. α/γ PSD Properties of DPA-DHS/PVT Samples

Figure 11 plots the 2D histograms of the PSD result (Q_{tail}/Q_{total}) versus energy for data acquired for the commercial EJ-299-34 material, while figs. 12 and 13 plot the same results for unshifted DPA-DHS/PVT samples and samples shifted with 0.05 wt. % Coumarin 6, respectively. The PSD figure of merit (FOM), defined as the separation between the two particle peaks over the sum of each respective FWHM, was measured as 2.43 using a 100 keV threshold energy for the EJ-299-34 data. This value is well above the threshold criterion for useful PSD performance established by Zaitseva et al. as a value of 1.27 [6]. The data shown in fig. 11 also supplements the results reported by Nyibule et al. for the α/γ PSD properties of the original EJ-299-33 plastic formulation [30]. Figure 14 plots the FOM results for both unshifted and shifted DPA-DHS/PVT samples plotted as a function of primary dye content, using the same 100 keV threshold energy. For the unshifted samples, while there is some increase in

Figure 11: $^{210}\text{Po}/^{137}\text{Cs}$ PSD plot of commercial EJ-299-34 plastic.

504 the FOM as the content is increased above 10 wt.%, the FOM trends toward a decrease
 505 above 20 wt.% and never is higher than 0.7. In contrast, the wavelength shifted samples
 506 show an approximately linear trend towards increasing FOM values, with the 50 wt.%
 507 sample displaying the highest obtained FOM value of 1.05, a value which is close to
 508 but less than the 1.27 threshold criterion. This is visually observable in fig. 13 that the
 509 α distribution is not cleanly separated from the γ branch, with a slight degree of overlap
 510 between the two. The significantly poorer performance of the unshifted samples can,
 511 like the light yield results, be largely be attributed to the self absorption by the DPA-
 512 DHS dye, although some of the effect is also directly attributable to the differences
 513 in the decay curves shown in fig. 10. Since the charge comparison method relies on
 514 the measurement of relatively low light levels in the tail of the pulse, any decrease of
 515 detectable photons attributable to self absorption will have a significant and detrimental
 516 effect on the achievable PSD performance of the material. This is further evidenced by
 517 the large decrease in apparent α energy that is observed with increasing dye content.
 518 For the 10 wt.% sample, the apparent energy of the alpha peak is less then that of
 519 EJ-299-34, with approximate values of 260 keV-ee and 320 keV-ee, respectively, and

Figure 12: $^{210}\text{Po}/^{137}\text{Cs}$ PSD plot of unshifted 50 wt.% DPA-DHS/PVT.

520 decreases down to approximately 170 keV-ee for the 50 wt.% sample. Since all of
 521 the energy of the incident α -particles is absorbed within a thin surface layer on the
 522 face of the samples opposite of the PMT, the emitted light must travel the maximal
 523 distance through the samples and is thus will experience a large and uniform degree of
 524 loss due to self absorption, as compared to excitation across the entire volume of the
 525 sample in the case of incident γ -particles. On the contrary, the apparent alpha energy
 526 of the wavelength shifted samples is largely unchanged as the content of DPA-DHS
 527 is increased, decreasing slightly from 250 keV-ee to 235 keV for the 10 and 50 wt.%
 528 samples, respectively.

529 There are potentially several factors that can contribute to the fact that the Coumarin
 530 6 shifted samples do not match the performance level of the commercial EJ-299-34
 531 plastic. From the photoluminescence spectra shown in fig. 7, it is obvious from the
 532 longer wavelength emission of the Coumarin 6 samples that the overall detection effi-
 533 ciency by the R878 PMT for scintillation photons is significantly lower as compared to
 534 EJ-299-34. Thus while the light yields of EJ-299-24 and the shifted 50 wt.% DPA-DHS
 535 are approximately the same, overall fewer photons are detected for the latter, which will

Figure 13: $^{210}\text{Po}/^{137}\text{Cs}$ PSD plot of Coumarin-6 shifted 50 wt.% DPA-DHS/PVT.

result in loss of precision in terms of quantifying the relatively small amounts of de-
 layed light emitted by the sample. However, given that the relative change in the slow
 component (going from γ to α excitation) of the scintillation delay for the 50 wt.%
 DPA-DHS sample was considerably less than that for EJ-299-34, as is shown in fig. 9
 and fig. 10, the relative PMT response alone is not enough to explain the poorer perfor-
 mance. As the emission of delayed fluorescence photons depends on the triplet-triplet
 annihilation process, which in turn depends on the diffusivity of triplet excitons within
 the material [31, 32], it is possible that a significant difference in triplet diffusivity may
 be one of the factors responsible for the decreased PSD performance. Given that crys-
 talline 9,10-diphenylanthracene is known to have good PSD performance [13–15], it
 is reasonable to presume that if a difference in triplet diffusivity is indeed responsible
 for the diminished performance, the structural modifications and/or polymer matrix
 of the DPA-DHS/PVT material are directly involved. Since the time scale for energy
 transfer from matrix to dye of triplet excitons should be much faster than the diffu-
 sion/annihilation process, non-radiative energy transfer to and from DPA cores should
 be the primary mechanism for triplet migration. In this sense, the polymer matrix, as

Figure 14: PSD figure of merits of both unshifted and Coumarin 6 wavelength shifted samples with DPA-DHS content from 10-50 wt.%.

well as the flexible linking groups that bind the DPA cores will combine to increase the average DPA core spacing, which in general should have the effect of decreasing the efficiency and overall rate of energy transfer, leading to an overall decreased triplet diffusivity. If this hypothesis is correct, then it is expected that both a further increase in DPA core content, as well as a reduction in the linking group chain length could lead to a significant increase in PSD performance. However, both of these measures are problematic in terms of sample preparation; in particular, reduction of the linking group chain length will surely lead to both lower solubility and higher melting point of the dye monomer, making fabrication of such a plastic with even higher loadings even more problematic, if not impossible;

4. Conclusion

A novel, highly soluble, and polymerizable diphenylanthracene-based dye (DPA-DHS) was successfully synthesized, and plastic scintillator samples fabricated using this dye monomer were found to be hard, durable, and highly transparent. Dye concen-

trations of at least 50 wt.% when copolymerized with PVT were found to be readily achievable. Of all of the DPA-DHS/PVT compositions tested, the Coumarin 6 wavelength 50 wt.% DPA-DHS was found to have the best performance, albeit notably less than the commercial EJ-299-34 plastic. While the unshifted DPA-DHS/PVT samples did show PSD properties, the strong effects of self-absorption led to significant loss of performance at the highest DPA-DHS concentrations. While the ultimate performance of the DPA-DHS/PVT material was just below the threshold limit for usability in real detectors, it does serve as a proof-of-concept for the possibility of highly loaded plastics stabilized via copolymerization, the lessons from which can be utilized in the design and synthesis of entirely new classes of dyes for PSD capable plastic scintillators. In doing so, it will be particularly important to focus on the design and synthesis of PSD-capable monomers that have shorter wavelength emission than the DPA-DHS monomer, so that they are compatible with traditional blue/violet emitting wavelength shifters, which is critical to achieving good spectral matching to typical PMT photocathodes.

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