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Matthieu Hamel, Stéphane Normand, Anne-Marie Frelin, Vesna Simic. Novel 1,8-naphthalimides for fast neutron/gamma discrimination in liquid scintillators. International Conference on Advances in Liquid Scintillation Spectrometry, May 2008, Davos, Switzerland. pp.13-18. <cea-05461808>

**HAL Id: cea-05461808**

**<https://cea.hal.science/cea-05461808v1>**

Submitted on 27 Jan 2026

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## NOVEL 1,8-NAPHTHALIMIDES FOR FAST NEUTRON/GAMMA DISCRIMINATION IN LIQUID SCINTILLATORS

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**ABSTRACT.** Several novel 4-substituted 1,8-naphthalimides were synthesized and used as fluorescent molecules for the preparation of liquid scintillators. Advantageously, these molecules exhibit a large Stokes shift, avoiding self-absorption processes and considerably simplifying the scintillator composition. Discrimination between fast neutrons and gamma rays was investigated by using the charge comparison method. This technique deals with the identification of neutrons from gamma rays by the shape of the light pulse delivered in the scintillator. The influence of naphthalimide substituents on the scintillator performances was examined. Only one blue fluorescing 4-substituted 1,8-naphthalimide showed an efficient discrimination capability. Light yields comparable to those of commercially available liquid scintillators were also observed.

### INTRODUCTION

Research in the field of scintillators has gradually increased in the last 2 decades, driven to a large degree by the rapidly growing needs of particle detectors for medical imaging, homeland security, radiation protection, and fundamental research. Among the different scintillating materials, liquid detectors have shown the most interesting properties in terms of particle discrimination. However, the presence of flammable, toxic, and explosive solvents hinders the use of these detectors for safety reasons. Recent studies have thus been directed towards the development of new solid scintillators. Among the promising candidates, polymers and composite materials are of special interest due to their low-cost potential and ease of manufacturing large-size samples. However, greater effort in the design of these new materials is necessary to achieve the same discrimination characteristics than those encountered with liquids.

In order to optimize the composition of our plastic scintillators and hence improve their performances, we have focused on the design and the characterization of fluorescent molecules exhibiting remarkable photophysical properties: 1,8-naphthalimides. In particular, derivatives substituted by electro-donating groups at the 4-position are known to display high fluorescence quantum yields and have tunable emission wavelengths (Alexiou et al. 1990). These molecules are also highly soluble in organic solvents or in commonly used monomers and exhibit a large Stokes shift, avoiding self-absorption processes as well as the use of a second solute to match the wavelength sensitivity range of the photodetector.

We report here our preliminary characterizations of several new fluorescent molecules dissolved in toluene. This solvent has been chosen because its chemical composition (H/C ratio) is very similar to that of polystyrene and polyvinyltoluene, the most important polymers for solid bulk and fiber scintillators. Thus, neutron sensitivity should be very close. Photophysical properties and discrimination abilities (neutrons versus gamma) were investigated. Particular attention was devoted to the study of the influence of naphthalimide substituents on particle detection.

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**EXPERIMENTAL DETAILS****General Procedure for the Synthesis of Substituted 1,8-naphthalimides**

Substituted 1,8-naphthalimides (**1–7**) were prepared according to known procedures (Hamel et al. 2008, 2009). The structure of these new molecules is shown in Figure 1.

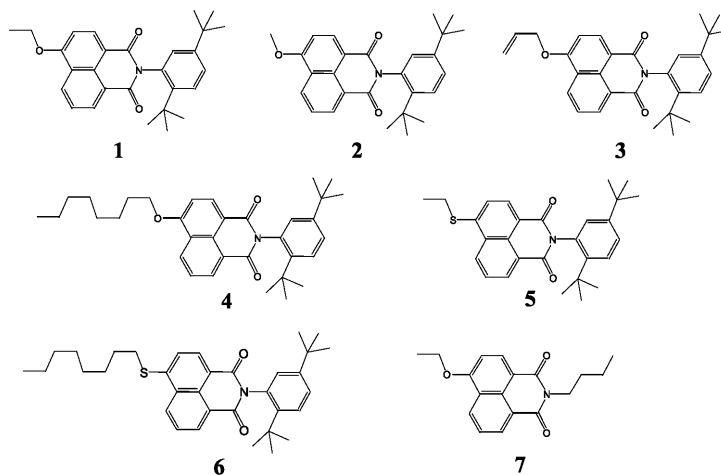


Figure 1 Structure of the 1,8-naphthalimide derivatives used in this study

Introduction of a bulky moiety on the naphthalimide chromophore is desirable to prevent from self-quenching effects, generally encountered at high fluorophore concentration. As already described in the literature (Le Barny et al. 2005), the 2,5-di-*tertio*-butylphenyl unit can be used for this purpose and leads to very high fluorescence quantum yield, even in solid matrices. All synthesized compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, FTIR spectroscopy, and elemental analysis.

**Physical Property Measurements**

Absorption and emission spectra were respectively recorded with a PerkinElmer Lambda 19 spectrometer and a Hitachi F-4500 spectrofluorimeter at room temperature. Fluorescence spectra were recorded with an excitation wavelength corresponding to the absorption maximum of the studied species.

The charge comparison method was chosen for  $n/\gamma$  discrimination measurement. This method lies in recognizing the light pulse shape delivered by the scintillator; gamma rays give short decay time pulses, whereas neutrons are known to induce a delayed fluorescence with longer decay times. Steps leading to this separation are gated pulse extraction and plotting-the-difference (Figure 2).

The total charge and the delayed charge (measured after the half maximum of the decay signal) were simultaneously recorded (Figure 2) and computed in a biparameter spectrum, which was normalized regarded to the total number of events.

Data were measured by using a QDC CAEN unit V465 in a VME crate. The signal from the PMT anode was then split in 2 parts by a passive splitter, one part giving the total charge and the second one delayed to give the charge of the tail of the pulse. The PMT last dynode signal was used to acti-

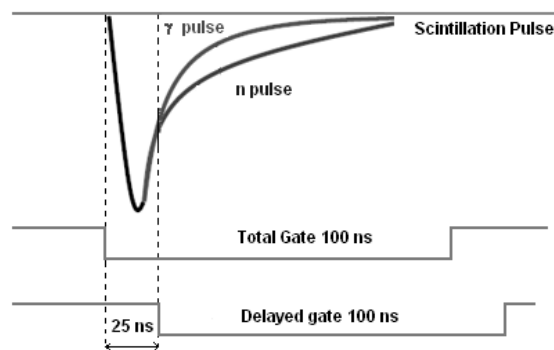


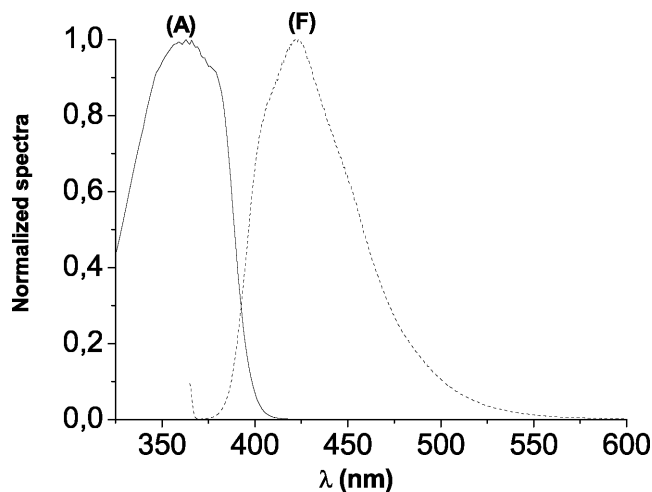
Figure 2 Timing diagram for the charge comparison method

vate the acquisition trigger. Discrimination measurements were made with a 74-kBq  $^{252}\text{Cf}$  source (about  $8800 \text{ n s}^{-1}$  / 17 keV, and 100–150 keV gamma rays) and a  $^{60}\text{Co}$  source of 100 kBq.

## RESULTS AND DISCUSSION

### Spectral Characteristics of 1,8-naphthalimides in Solution

The absorption spectrum of *N*-(2',5'-di-*t*-butylphenyl)-4-ethoxy-1,8-naphthalimide **1** presents a maximum at 363 nm corresponding to a  $S_0-S_1$  ( $\pi-\pi^*$ ) transition. The molar extinction coefficient  $\epsilon$  is equal to  $33,600 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The emission maximum is located around 425 nm (Figure 3), which is therefore ideally suited for the photocathode wavelength sensitivity (Photonis XP2020).

Figure 3 Normalized absorption (A) and fluorescence (F) spectra of compound **1** in toluene ( $0.2 \text{ g L}^{-1}$ ).

Advantageously, the large Stokes shift observed ( $\Delta\nu = 4248 \text{ cm}^{-1}$ , i.e. 65 nm) avoids self-absorption process and simplifies considerably the scintillator composition since no wavelength shifter is needed, as compared with the complex mixtures of commercial scintillators. This is particularly important for large-volume scintillators as well as in scintillating fibers for tracking detectors (Barni

et al. 1997). The importance of reducing self-absorption effects in scintillators by employing solutes with large Stokes shifts was stressed in the past by Renschler and Harrah (1985).

Spectral properties of the other fluors (**2–7**, Figure 1) are comparable to those of compound **1** (Hamel et al. 2008). Sulfur-containing derivatives exhibit a slight bathochromic shift of absorption and emission maxima ( $\lambda_{\text{max}}^{\text{Abs}} = 390\text{nm}$ ) and ( $\lambda_{\text{max}}^{\text{Em}} = 445\text{nm}$ ), as expected (Valeur 2002).

### Scintillation Properties

A comparative study of n- $\gamma$  discrimination by the charge comparison method was carried out for these 7 novel fluors. This technique leads to the 2-dimensional spectra presented in Figure 4, obtained by plotting the delayed charge (measured over the half of the signal fall) as a function of the total charge recorded. When discrimination occurs, a separation between neutron (upper) and gamma rays (lower) events is then observed (see Figure 4a).

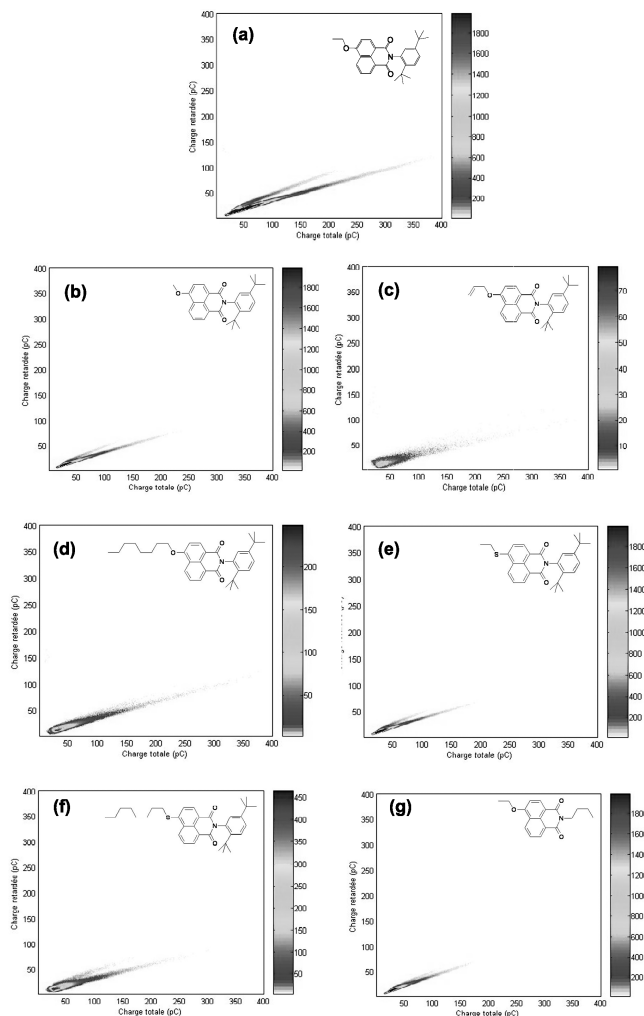


Figure 4 n- $\gamma$  discrimination observed with several substituted 1,8 naphthalimides solubilized in toluene ( $10\text{ g L}^{-1}$ ).

As shown in Figure 4, discrimination capability is not systematically observed. Only one blue fluorescing 4-substituted 1,8-naphthalimide (compound **1**) exhibits this characteristic despite the same experimental setup. Both substituents of the chromophore (located either on the 4- or the *N*- position) seem to be of importance to discriminate neutron from gamma radiations in liquids. Complementary characterizations are necessary to better understand relationship between structures and properties observed and hence optimize the composition of our future plastic scintillators.

The light output of our most efficient formulation was compared to other commercially available products (BC-501A [Bicron], NE213 [Saint-Gobain], or Ultima Gold AB [PerkinElmer]). All samples were all bubbled with argon. The influence of the solvent nature on the light yields was also examined.

The results, listed in Table 1, are all normalized to a *p*-terphenyl/POPOP/toluene system. BC-501A, comprised of 90% of xylene and other chemical compounds, exhibits a comparable light output to our system. When xylene is used as solvent, a closer value is obtained, therefore illustrating the importance of the solvent nature in the scintillating process.

Table 1 Light yields comparisons

Liquid scintillator <sup>a</sup>	Light output (%) <sup>b</sup>
<i>p</i> -terphenyl/POPOP (4/0.1 g/L) in toluene	100
NE213	85
Ultima Gold AB	77
BC-501A	64
1,8-naphthalimide / <i>m</i> -xylene	64
1,8-naphthalimide / toluene	59
1,8-naphthalimide / mesitylene	56
1,8-naphthalimide / benzene	51
1,8-naphthalimide / <i>p</i> -xylene	50
1,8-naphthalimide / <i>p</i> -isopropylbiphenyl	33
1,8-naphthalimide / styrene	8

<sup>a</sup>10 g/L of naphthalimide **1** in the corresponding solvent.

<sup>b</sup>Normalized to 100 for scintillator reference.

One can also notice that styrene is not an appropriated “solvent” since weak light output was measured. This is due to a less energetic yield transfer between this compound and the 1,8-naphthalimide **1** in non-radiative interaction.

## CONCLUSIONS

We have shown that dissolved 4-substituted 1,8-naphthalimides can be used as scintillating molecules, exhibiting relatively high light output, comparable to those of commercially available liquid scintillators and emitting in the high sensitivity wavelength region of the photodetector. For one of these compounds, n- $\gamma$  discrimination ability was observed by applying the charge comparison method. It was shown that both substituents located on 4- and *N*-positions of the chromophore core were of importance. The reasons of these effects are still under study.

**ACKNOWLEDGMENTS**

The research was enabled by financial contributions from the French government through the French National Research Agency (ANR)/Programme National de Recherche Blanc, NEUTROMANIA.

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