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Matthieu Hamel, Mathieu Trocmé, Adrien Rousseau, Stephane Darbon. Red-emitting liquid and plastic scintillators with nanosecond time response. Journal of Luminescence, 2017, 190, pp.511-517. 10.1016/j.jlumin.2017.06.012 . cea-01803831

## HAL Id: cea-01803831 https://cea.hal.science/cea-01803831

Submitted on 7 Jul2023

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## Red-emitting liquid and plastic scintillators with nanosecond time response

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#### Abstract

Due to the extreme experimental conditions encountered, the Laser Mégajoule facility (LMJ) needs to develop and characterize new organic scintillators with unseen features: a fast decay time, in the order of one nanosecond with almost no afterglow, and an emission wavelength in the red region, typically more than 600 nm.

Thus, various compositions have been evaluated, prepared and tested. The materials are composed of a matrix (either liquid or plastic) embedding two fluorophores and a light quencher. Time-Correlated Single Photon Counting was used to assess the main criteria of the materials, which is their photoluminescence decay. In the liquid state, ultra-fast materials were successfully prepared. One liquid scintillator formulation showed the following characteristics: an emission wavelength > 600 nm, a mean decay time of 0.84 ns with a FWHM pulse width of 1.92 ns. In the plastic state the preparation was less straightforward. A plastic scintillator with emission wavelength > 600 nm, a decay time < 7 ns with a FWHM of 8.60 ns was obtained. We have verified that the best plastic sample does not present any afterglow. A light yield around 200 ph/MeV has been estimated from relative radioluminescence measurements, this value being around 4 times lower than the BC-422Q 2%, quenched plastic scintillator.

#### Keywords

Organic scintillator; Time-Correlated Single Photon Counting; Radiation Measurement; Fluorescence; Laser Mégajoule.

#### Introduction

The Laser Mégajoule facility is a large laser-based inertial confinement fusion (ICF) research device built in France. Not less than 176 laser beamlines impinge a hohlraum which contains a deuteriumtritium fusion target. This target may explode through X-rays heating, liberating thus various ionizing radiations such as gamma and X-rays, fast prompt neutrons and delayed neutrons. As the gamma burst is rapidly followed by neutrons, nanosecond time-resolved detectors are required. In addition, parasite Cherenkov light occurring inside the measurement systems prevents the use of blue-

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sensitive instruments. This explains the need to red-emitting, fast decay time plastic scintillators. Such detectors are to be installed as a diagnostic on the LMJ [1].

To the best of our knowledge, no commercial supplier can offer a plastic or scintillator displaying such characteristics, and only a few publications report them. BC-422Q (Saint-Gobain Crystals and Detectors) and EJ-232Q plastic scintillators (Eljen Technology) are commercially available, but are only UV-emissive materials. Usually quenched with benzophenone at different concentrations, they have been extensively studied by Moszińsky et al [2]. Liquid and plastic scintillators are always composed of a matrix embedding several fluorophores, and in the field of fast scintillators various chemical elements can be added for such a goal and many others [3]. In any case, a decrease of the scintillation decay time always comes with a strong decrease of the scintillation efficiency as well [2]. Addition of oxygen to the solution leads to the quenching of the slow component [4]. Alkyl and aryl amines, alkyl and aryl halogens [5] as well as heavy metals [6] have also been reported.

Noteworthy was the work by Flournoy and Lutz which managed to combine red emission and fastness, at least in a liquid medium [7]. Their strategy consisted in adding the dyes at very high concentration to allow the fastness in the liquid scintillator, probably by self-quenching. An extensive study was performed on the nature and the concentration of the secondary dye, yielding to materials with emission wavelengths as high as 735 nm. All this was made possible thanks to the use of polar solvents such as benzonitrile or benzyl alcohol, the latter being unusually encountered in liquid scintillation counting.

Ultimately, only a single publication refers to fast and red scintillator in the plastic state [8]. A polystyrene monolith containing butyl-PBD, dimethylPOPOP and perylene and rubrene was exposed to important irradiation doses as high as 240 Gy. Such a treatment allowed the material decay time to decrease from 35 ns to 5 ns, but this is unfortunately too slow for our needs.

#### Materials and methods

All chemicals were purchased from Sigma-Aldrich. Spectroscopic toluene was obtained from Carlo Erba. SP32 plastic scintillator was obtained from NUVIA CZ. EJ-200 plastic scintillator was obtained from Eljen Technology. BC-422 plastic scintillator and its quenched derivatives were bought to Saint-Gobain Crystals and Detectors. All the monomers and amines were vacuum-distilled prior to the experiment.

Fluorescence spectra were recorded with a Horiba Jobin Yvon Fluoromax 4P spectrofluorometer (Horiba Jobin Yvon), monitored with FluorEssence software. The light decay characteristics of the liquid and plastic scintillators were investigated with the Time-Correlated Single Photon Counting (TCSPC) module available as an option on the device. Two different excitation wavelengths were used, 274 nm and 368 nm, allowing us to evaluate the impact of the quencher on the first and the second fluorophore, respectively. The TCSPC analysis was performed in 3 cm<sup>3</sup> quartz cuvettes with the emission recorded at 90° from the excitation diode. Plastic scintillators were excited on their cylindrical edge, the flat face being directed towards the photodetector of the spectrofluorometer. Decay spectra were fitted using the DAS6 software (Horiba Jobin Yvon). Radioluminescence spectra were acquired by using the following procedure. In the Fluoromax 4P spectrofluorometer, the excitation light was shut down. In the center of the experiment chamber, <sup>90</sup>Sr/<sup>90</sup>Y  $\beta$  emitting radioactive source (37 MBq) was placed in close contact with the scintillator, the opposite side of the latter which was facing the detection cell. Spectra were acquired with integration time 0.1 s/nm.

#### Experimental

Liquid scintillators were prepared by dissolving the dyes into spectroscopic toluene. No other scintillation solvent was studied. Once prepared, the solutions were neither degassed nor saturated with neutral gas. The reason is twofold: the presence of oxygen decreases the decay time, and the saturation with neutral gas is modified by slow oxygen diffusion within the liquid.

Plastic scintillators were prepared according to our internal, standard procedure. When necessary, the matrix was cross-linked (see results). After heating the monomers containing the suitable molecules until complete polymerization, the raw material was cut and polished until obtaining a plastic scintillator with dimension 49 mm diameter and 10 mm thickness.

#### Results

This work requires both chemical and photophysical expertise. To prepare these materials, we started developing the formulations in the liquid state, as it goes faster to mix powders in liquids rather than waiting for a full polymerization and machining the raw plastic scintillator. However, the analogy between liquids and plastics is not total. For example, oxygen-saturation or solvent quenching effects are different in both states, so we decided to use the organic quencher strategy.

The scintillation system can be described as follows: a matrix, being either liquid or plastic, one or two fluorescent molecules, a primary dye which absorbs UV photons and emits light in the 365 nm range, and a suitable wavelength shifter to reach the desired wavelength, i.e. more than 550 nm. Added to these molecules are organic quenchers and if necessary a cross-linker and a polymerization initiator when the materials to be prepared are plastics.

#### Liquid scintillator

To determine the most suitable composition, we used the following strategy: ① selection and determination of the best concentration of the primary fluorophore, ② nature and concentration of the secondary fluorophore, alone, then in addition with the primary fluorophore, ③ nature and concentration of the quencher. Pragmatically, we started with systems as simple as one fluorescent molecule (herein called the primary dye) in spectroscopic toluene. Various molecules can act as a primary fluorophore. Lots of them have already been tested in regular liquid scintillation counting and often new molecules appear in the literature [3]. According to literature precedents [9], we have checked the influence of the 2,5-diphenyloxazole (PPO) concentration on the luminescence decay, and only the results of this primary fluorophore are presented herein, as PPO seems to be the fastest decaying compound according to our internal comparisons.

To analyze the decay time of a scintillator, the choice of Time-Correlated Single Photon Counting is obvious. An excitation with a radiation would require a sophisticated setup not suitable for analyzing a large number of samples [4]. So the choice of excitation diodes coupled to a spectrofluorometer is a powerful and reliable solution. In addition, we have the possibility to excite the material at two different wavelengths, 274 nm and 368 nm. Assuming the fact that at the lowest excitation wavelength the primary fluorophore absorbs more than the second, the first excitation wavelength allows us to study the behavior of the whole system (excitation in the absorption band of the matrix), whereas the second excitation diode excites only the last fluorophore. By comparing the response of the material excited either at 274 nm or 368 nm, it is possible to determine where potentially the system matrix-fluorophores could be time-limited by one or several chemicals. This ultimate mesurande of the whole system will be the key parameter in the discussion section. Figure 1 shows the influence of the PPO concentration on the luminescence decay time and the Table 1 resumes the first set of experiments including potential quenchers. The decay part of the pulse

signal is fitted as the sum of two exponentials, given as  $A(t) = A_0 \left[A_{fast}^{\left(e^{-t/\tau_{fast}}\right)} + A_{slow}^{\left(e^{-t/\tau_{slow}}\right)}\right]$ . In the context of this document, the following annotation will be used, as  $\tau_{fast}$  (%) +  $\tau_{slow}$  (%) in ns, for the fast and the slow components, respectively. A mean value  $\tau_{mean}$  (each exponential being weighted by its respective percentage) is also reported to simply represent the photoluminescence decay.

Starting with commercial materials, we have confirmed the good agreement of our experimental setup with commercial, reported data. EJ-200 and SP32 which are regular scintillators display almost monoexponential decays, with values of 2.4 and 2.9 ns, respectively (2.1 and 2.5 ns from the commercial datasheets). Doing the same with fast materials – the BC-422 series – show samples with decay time less than one nanosecond. All the values are biexponential, with generally a residual in the range of 3 ns. The measured fast decay values are 1.60, 0.88 and 0.88 ns for BC-422, Q 1% and Q 2% respectively, with commercial values given as 1.6, 0.7 and 0.7 ns, therefore in good agreement.

From Table 1, one can see that low PPO-concentrated liquids are in fact the fastest materials. This is in disagreement with the observations reported in ref. [9, see Figure 5]. We have no explanation for this. Highly PPO-concentrated liquids such as sample #6 see the appearance of a long-life photoluminescence. Our interpretation is that a large concentration of fluorophores such as PPO can lead to multiple emission-reabsorption steps along the track of the light, therefore potentially increasing its decay time. Another possibility is the creation of excimers of PPO, with longer decay times. At this stage of the experiment the efficiency of benzophenone to quench light emanating from PPO is noteworthy: only 1 wt% leads to a sub-ns liquid scintillator (sample 8).

Reference	PPO concentration (wt%)	Quencher (wt%)	τ <sub>fast</sub> (%) + τ <sub>slow</sub> (%) (ns)	τ <sub>mean</sub> (ns)	FWHM (ns)
EJ-200	Proprietary	-	2.38 (90) + 16.4 (10)	3.78	4.60
SP32	Proprietary	-	2.95 (87) + 14.7 (13)	4.48	5.59
BC-422	Proprietary	-	1.60 (83) + 3.38 (17)	1.90	2.85
BC-422Q 1%	Proprietary	Benzophenone (1)	0.88 (69) + 3.15 (31)	1.58	2.22
BC-422Q 2%	Proprietary	Benzophenone (2)	0.88 (68) + 2.86 (32)	1.51	2.17
1	0.5	-	2.27 (81) + 4.51 (19)	2.69	4.39
2	1.0	-	1.74 (32) + 4.10 (68)	3.34	4.00
3	2.0	-	1.67 (28) + 4.86 (71)	3.91	3.68
4	4.8	-	1.04 (10) + 6.06 (90)	5.56	3.57
5	10	-	0.64 (3) + 7.54 (97)	7.33	3.66
6	28	-	0.50 (2) + 11.03 (98)	10.82	10.20
7	0.5	Piperidine (1)	0.79 (69) + 3.31 (31)	1.57	3.62
8	0.5	Benzophenone (1)	0.56 (81) + 2.06 (19)	0.84	1.92

Table 1. Toluene-based liquid scintillators #1 – 8 compared with standard plastic scintillators from various suppliers.  $\lambda_{ex} = 274 \text{ nm}$ .  $\lambda_{obs}$  at the maximum of the emission for each material.

 $\tau_{mean} = \%_{fast} \times \tau_{fast} + \%_{slow} \times \tau_{slow}.$ 



Figure 1. Influence of the PPO concentration on the luminescence decay time, fitted as a biexponential sum. The size of the ball represents the ponderation of the fast or slow value.

Following the search for the best PPO concentration, a secondary fluorophore was added to allow reaching higher emission wavelengths, namely more than 580 nm in our case. As it is established the Förster energy transfer between acceptors and donors to give an efficient organic scintillator [10], we preferred shortening the multiple transfer pathways by linking the emission of the PPO directly to a red-emissive dye, hoping the the transfer could occur as well.

The following secondary dyes were compared: Rhodamine 610 perchlorate, 4-(Dicyanomethylene)-2methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM), cresyl violet perchlorate, resorufin, Nile red (NR), and pyrromethene 605. Most of these molecules are already used as laser dyes. They are drawn in the Figure 2.



Figure 2. Red emissive dyes used in this study.

Since Nile red showed to be the most sensitive molecule to the presence of quenchers, only the results with this dye are reported. Two different Nile red concentrations were tested: 0.02 wt% and 0.1 wt% respectively in toluene, and piperidine as a quencher was potentially added. The results are given in the Table 2.

Table 2. Photophysical properties of toluene-based Nile red (NR) solutions at two different concentrations, potentially quenched with piperidine (fluorescence:  $\lambda_{ex} = 250$  nm; TCSPC:  $\lambda_{ex} = 274$  nm,  $\lambda_{ob} = 600$  nm).

Reference	Composition in toluene	$\lambda_{em}^{max}$ (nm)	I <sub>fluo</sub> (counts)*	τ <sub>fast</sub> (%) + τ <sub>slow</sub> (%) (ns)	τ <sub>mean</sub> (ns)	FWHM (ns)
9	NR (0.02 wt%)	602	1	7.59 (100)	7.59	8.31
10	NR (0.02 wt%) + piperidine (4 wt%)	604	0.107	1.55 (96) + 6.6 (4)	1.75	2.58
11	NR (0.1 wt%)	624	0.941	6.1 (100)	7.59	11.85
12	NR (0.1 wt%) + piperidine (4 wt%)	638	0.048	1.87 (87) + 4.5 (13)	2.21	3.02

\* set to one for sample #9.

Whereas the most concentrated solution of Nile red is also the fastest, upon addition the apparent decay time  $\tau_{mean}$  is the fastest for the lower concentration, namely 0.02 wt%. Also, upon addition of up to 4 wt% of piperidine, the FWHM is the lowest for sample 10, which is the less concentrated in Nile red. It is noteworthy the strong hypochromic effect on the residual fluorescence, as approximately 10% of photoluminescence remains (see the fluorescence intensity in the Table 2). The bathochromic effect is more pronounced for the highest concentration, with 14 nm shift value, probably due to the reabsorption of Nile red.

Now that potential quenchers have been found for the primary, then for the secondary fluorophore, both dyes were coupled into the same liquid. Several other amine derivatives were evaluated as potential quenchers for Nile red, from primary to quaternary amines. At last, benzophenone was also tested. Their structure is drawn in the Figure 3, and the quenching results are resumed in the Table 3.



Figure 3. Potential quenchers "Q" for the Nile red dye: amines and benzophenone.

Table 3. Quenching effect of various amines on a toluene-based solution of PPO (0.5 wt%) and Nile red (0.02 wt%). TCSPC:  $\lambda_{ex} = 274 \text{ nm}, \lambda_{ob} = 600 \text{ nm}.$ 

Reference	Quencher (wt%)	τ <sub>fast</sub> (%) + τ <sub>slow</sub> (%) (ns)	τ <sub>mean</sub> (ns)
13	None	5.95	5.95
14	Dodecylamine (4)	5.25	5.25
15	Piperidine (4)	1.66 (97) + 34.1 (3)	2.63
16	Hünig base (4)	1.50 (75) + 2.74 (25)	1.81
17	Hünig base (12)	0.82 (55) + 2.50 (45)	1.58
18	Hünig base (16)	0.75 (43) + 2.57 (57)	1.79
19	N,N-dimethylaniline (4)	1.20 (27) + 8.75 (73)	6.71
20	N,N-dimethylaniline (8)	1.23 (18) + 8.73 (82)	7.38
21	Pyridine (4)	4.65 (80) + 7.48 (20)	5.21
22	DMAP (4)	6.56	6.56
23	Bu₄NBr (4)	5.01	5.01
24	Benzophenone (1)	6.10	6.10

Table 4. TCSPC of samples 15 and 24 at various excitation and observation wavelengths.

Reference	λ <sub>ex</sub> (nm)	λ <sub>ob</sub> (nm)	τ <sub>fast</sub> (%) + τ <sub>slow</sub> (%) (ns)	τ <sub>mean</sub> (ns)
15	274	380	0.52 (63) + 1.86 (37)	1.01
15	274	600	1.66 (97) + 34.1 (3)	2.63
15	368	600	1.53	1.53
24	274	380	0.71 (68) + 1.84 (32)	1.07
24	274	600	6.10 (100)	6.10
24	368	600	5.70 (100)	5.70

The main photophysical processes occurring during the quenching of an excited state  $M^*$  with a quencher Q are: collision with a heavy atom; electron, proton or energy transfer; and excimer or exciplex formation [11]. Tetrabutyl ammonium bromide was expected to be an efficient quencher thanks to the presence of the heavy bromine atom. In fact, no quenching was observed (entry 23). Dodecylamine, DMAP and benzophenone did not afford any quenching effect as well. The quenching effect is still unclear to our eyes.

The data provided in the Table 4 give many information when linked altogether.

- The PPO deexcitation is seen when exciting at 274 nm and observing at 380 nm,
- The Nile red deexcitation is seen when exciting at 368 nm and observing at 600 nm,
- The whole system is probed when exciting at 274 nm and observing at 600 nm.

Thus, it is possible to associate a suitable quencher/fluorophore couple. Sample 15 uses piperidine as a quencher. In our conditions, the decay time of the piperidine/PPO couple is 1.01 ns (quenched) and the decay time of the piperidine/NR couple is 1.53 ns (quenched). The whole system is 2.63 ns, which is rather fast. When benzophenone is used as the quencher in the sample 24, the decay time of the piperidine/PPO couple is 1.07 ns, so in the range of the piperidine/PPO couple. However, the decay time of the benzophenone/NR couple is 5.70 ns, which is in the same range as the reference 9 (NR only in toluene) from Table 2. The resulting decay time of the whole system (6.10 ns) is limited by this slow decay time. We can therefore conclude that benzophenone is an efficient quencher of PPO excitons only, and NR is not affected.

#### Plastic scintillator preparation and characterization

Based on these results, we transferred the best liquid formulation into a plastic matrix. Only quenchers such as piperidine and the Hünig base were considered. Table 5 resumes the different preparations.

Reference	Polymer*	PPO (wt%)	Nile red (wt%)	Quencher (wt%)	AIBN (wt%)	
1	PS	0.5	0.02	Piperidine (4)	-	
2	PS	-	0.02	Piperidine (4)	-	
3	PS	0.5	0.02	Hünig (4)	-	
4	PS	-	0.02	Hünig (4)	-	
5	CL-PS	0.5	0.02	Hünig (4)	-	
6	CL-PS	-	0.02	Hünig (4)	-	
7	CL-PS	0.5	0.02	Hünig (2)	-	
8	CL-PS	0.5	0.02	Hünig (4)	0.1	
9	CL-PS	-	0.02	Hünig (4)	0.1	
10	CL-PS	0.5	0.02	Hünig (2)	0.1	

\* PS stands for polystyrene; CL-PS for a cross-linked polystyrene derivative.

All our attempts to incorporate and stabilize the piperidine inside the material failed. Due to its low boiling point (106°C), piperidine is rejected from the mixture while heating due to evaporation. We therefore focused our attention on the Hünig base (*N*,*N*-diisopropylethylamine) whose boiling point is slightly higher: 127°C. It is noteworthy that both molecules have the expected effect on the photoluminescence, which is the quenching of the long state luminescence. Unfortunately, it was noticed that they are efficient polymerization inhibitors. As an example, more than a month of heating was required to terminate the polymerization of samples #1 - 4. Thus, we decided to cross-link the polymer, allowing therefore an increase in the polymerization kinetics, as well as an increase of the apparent mechanical strength. Ultimately, AIBN was added to the mixture for a better polymerization process.

Unfortunately, the last attempts (samples 5 to 10) led to an uncontrollable polymerization which led to demixtion and heterogeneous mixtures. Samples #1 - 4 are visible on the Figure 5. Their decay time was checked: Table 6 shows that their decay time was longer than expected.

From the fluorescence spectra displayed in Figure 4-left, one can see the significant effect of the PPO addition to the mixture. With an excitation wavelength of 270 nm, corresponding mainly to the excitation wavelength of the polystyrene, we can have somehow an overview of the emission behavior of the sample. Thus, materials #1 and #3 which do contain PPO show a significant increase of the luminescent response compared to their equivalent PPO-unloaded samples. This leads to materials which are three to four times more luminous when PPO is present. In addition, the Förster energy transfer between PPO and Nile Red is not efficient enough as a residual fluorescent signal can be seen in the 360 nm region for samples #1 and #3. We currently have no explanation about the bathochromic shift between samples #2 and #4 where the emission maximum goes from 622 up to 630 nm. TCSPC of the samples (Figure 4-right) show interesting features. Unfortunately, none of them are sub-nanosecond samples and their decay time is in the range 8 - 13 ns. The fastest samples are #1 and #2. However, sample #2 has a fastest rise time compared with #1, which impacts the FWHM of the pulse width at its benefit, giving a material with a FWHM around 5.60 ns. This can be attributed to the addition of PPO in the sample #1. It is noteworthy that the commercial BC-430, redemissive plastic scintillator is rather slow, with a reported decay time of 16.8 ns and a FWHM pulse width of 17.7 ns [12].



Figure 4. Left: Fluorescence spectra of samples 1 - 4 ( $\lambda_{ex} = 270$  nm). Right: TCSPC of samples 1 - 4.

Table 6. Photoluminescence properties and TCSPC of the samples 1 - 4;  $\lambda_{ex} = 274$  nm,  $\lambda_{ob} = 600$  nm.

Reference	$\lambda_{em}^{max}$ (nm) ± 1 nm	I <sub>fluo</sub> (counts)*	τ <sub>fast</sub> (%) + τ <sub>slow</sub> (%) (ns)	τ <sub>mean</sub> (ns)	FWHM (ns)
1	628	1	6.7 (94) + 39.6 (6)	8.67	8.61
2	622	0.28	7.5 (94) + 39.4 (5)	9.41	5.60
3	634	0.85	7.4 (85) + 27.4 (15)	10.4	13.06
4	630	0.34	9.5 (88) + 41.4 (12)	13.3	9.66

\* set to 1 for sample 1.



Figure 5. Picture of the four plastic scintillators #1-4, which display the same visual shape.

According to the different mechanisms occurring between the excited state  $M^*$  and Q, it is most probable that the huge discrepancy between liquid and plastic scintillators comes from the molecular motion. The low concentration of the molecule to be quenched (herein the secondary fluorophore) coupled with its stationary state may preclude any quenching effect occurring from the amine Qduring the lifetime of the exciton  $M^*$ . Again, the TCSPC analysis shows that only the Nile red is not quenched: with  $\lambda_{ex} = 274$  nm and  $\lambda_{ob} = 370$  nm parameters (so visualization of the PPO behavior), a fast  $\tau_{mean} = 4.16$  ns decay time is observed (1.69 (59%) + 7.73 ns (41%), as a biexponential decay), whereas a  $\lambda_{ex} = 368$  nm and  $\lambda_{ob} = 620$  nm parameters give a  $\tau_{mean} = 7.17$  ns of the Nile red.

#### Radioluminescence

To determine the light yield, several methods are available but we decided once again to use a spectrofluorometer-based solution. Ultrafast plastic scintillators are known to be poorly-emissive while exposed to ionizing radiations. Except when absolute light yield of a scintillator has to be determined, a relative light yield can only be performed between samples with approximately the same emission wavelength, due to the wavelength-dependent quantum efficiency of photomultiplier tubes. In this context our radioluminescence setup benefits from the monochromator and the associated response curve of the spectrofluorometer. By using a beta-decaying strontium-yttrium radioactive source, we can simulate the behavior of a scintillator exposed to ionizing radiations. Thanks to the monochromator, the response is linear whatever the emission wavelength, therefore we can compare our materials relative to known samples but with different emission wavelengths, provided that all the samples are of same size and volume.

The data presented in the Table 7 show that relative to a slightly bigger BC-422Q 2% scintillator ( $\phi$  48 mm, h 15 mm), the light yield is ca. 300 ph/MeV for the best sample, herein #3, so approximately 2 times lower than the commercial plastic scintillator BC-422Q 2%. Samples #1 and #3 showed a residual amount of PPO emission, as was already noticed in the fluorescence spectra (Figure 4, left). And again, a beneficial effect of PPO was noticed, as the relative light yield was 2 to 4 times higher when the scintillators were loaded with the primary fluorophore.

Sample	$\lambda_{em}^{max}$ (nm)	Radioluminescence integral (%)*	Relative light yield (ph/MeV)
BC-422Q 2%	406	98.1 - 100	760
1	620	19.4 - 20.8	160
2	610	7.7 – 8.7	70
3	618	37.6 – 38.6	300
4	616	8.9 - 10.3	80

Table 7. Maximum of emission and relative light yield of samples #1 – 4 according to the BC-422Q 2% plastic scintillator.

\* The same experiment was repeated three times, 100% corresponds to the best measurement of a BC-422Q 2% sample. Light yield of BC-422Q 2% is 5% that of anthracene, giving ca. 760 ph/MeV [13].

#### Afterglow

Another required property for the material is the absence of any residual light which is so-called afterglow. The decay time of our fastest material (namely #1) was recorded with a 274 nm excitation wavelength on a 1600 ns range. Given a maximum value of 10000 counts, there were only 12 - 15 counts remaining after 100 ns, showing that the material has no light remanence.



Figure 6. TCSPC of sample #1, showing that almost no luminescence is remaining after 100 ns.  $\lambda_{ex} = 274$  nm,  $\lambda_{obs} = 600$  nm.

#### Conclusion

The goal of this work is to provide fast-decaying, red-emitting plastic scintillator formulations. Based on preliminary results, we demonstrated that nanosecond range liquid scintillators can be readily obtained: when the system was quenched with the Hünig base, a 1.58 ns decay time was reached. Interestingly, benzophenone revealed to be able to quench the PPO but not the Nile red. The formulation translation from the liquid to the solid state was not straightforward. Particularly the significant effect of the quencher on the polymerization process precludes the access to nanosecond decaying plastic materials. So far, the plastic scintillator showed the following characteristics: 620 nm emission wavelength, 8.6 ns decay time and a 160 ph/MeV relative light yield. Further work will be performed to evaluate various quencher/fluorophore couples for potential improvements. Next step will be to further characterize the materials under gamma excitation, then they will be adapted to the LMJ requirements.

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