



HAL
open science

Structural Variation of Carbazole Derivatives for Plastic Scintillation Applications

Eva Montbarbon, Fabien Sguerra, Guillaume H. V. Bertrand, Sylvain Gaillard, Jean-Luc Renaud, Robert B. Pansu, Matthieu Hamel

► **To cite this version:**

Eva Montbarbon, Fabien Sguerra, Guillaume H. V. Bertrand, Sylvain Gaillard, Jean-Luc Renaud, et al.. Structural Variation of Carbazole Derivatives for Plastic Scintillation Applications. *ChemPhotoChem*, 2017, 1 (10), pp.451 - 458. 10.1002/cptc.201700055 . hal-01633175

HAL Id: hal-01633175

<https://hal.science/hal-01633175v1>

Submitted on 6 Feb 2025

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Structural Variation of Carbazole Derivatives for Plastic Scintillation Applications

Eva Montbarbon^{a,b,c}, Fabien Sguerra^a, Guillaume H. V. Bertrand^a, Sylvain Gaillard^d, Jean-Luc Renaud^d, Robert B. Pansu^b, Matthieu Hamel*^a

^a CEA, LIST, Laboratoire Capteurs et Architectures Electroniques, 91191 Gif-sur-Yvette, France

^b Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires (CNRS UMR 8531), École Normale Supérieure de Cachan, 61 Avenue du Président Wilson, 94235 Cachan cedex, France

^c Doctoral School INTERFACES, Paris-Saclay University, 91400 Saclay, France

^d Normandie University, LCMT, ENSICAEN, UNICAEN, CNRS, 14050 Caen, France

Abstract

The preparation of various plastic scintillators with embedded carbazole moieties is reported. As a result of their versatility and advantageous luminescence properties, this system is a candidate of choice for such applications. Through careful system design, the carbazole in the system can have a variety of functions, for example as the polymer matrix, as the primary fluorophore or as the secondary fluorophore. For systems in which carbazole is embedded in the polymer matrix, poly(*N*-vinylcarbazole) (PVK) and poly(styrene-*co*-*N*-vinylcarbazole) were prepared by bulk radical polymerization. For application as a primary or secondary fluorophore, *N*-(2-ethylhexyl)carbazole (EHCz) is a particularly suitable molecule. When used at a low concentration it can act either as a primary fluorophore (when coupled with 1,4-bis(5-phenyloxazol-2-yl) (POPOP) or bis-(2-methylstyryl)benzene (bis-MSB) as the wavelength shifter), or as both primary and secondary fluorophore if the concentration inside the polymer matrix is high. The performance of EHCz was compared with the related molecule *N*-(ethyl)carbazole. Finally, another carbazole-containing molecule 2,4,5,6-tetrakis(carbazol-9-yl)-1,3-dicyanobenzene was loaded in a polymer matrix as the secondary fluorophore. Scintillation results show its efficiency to shift the scintillation response to wavelengths close to 500 nm. The preparation and primary photo-physical properties of each of these new plastic scintillators was reported, in addition to the scintillation properties of each. These results highlight the potential application of carbazole derivatives as fluorophores for nuclear detection.

1 Introduction

Since the beginning of this century, important breakthroughs have been reached regarding chemical modification of plastic scintillators [1]. Although in the past the catalogues of commercial suppliers were almost fully composed of plastic scintillators showing various emission wavelengths, now there is significant interest in tuning the scintillator's response towards a given type of radionuclide, for example, for fast or thermal neutrons [2]. In this context, a new, chemically modified plastic scintillator was recently proposed by a manufacturer named Eljen Technology [3]. A second important challenge would be to perform efficient gamma spectroscopy with such materials, whose density and effective atomic number usually prevent them from such application [4].

Regardless of whether the scintillator is plastic or liquid in nature, it is basically composed of a matrix (polymer or organic solvent) where one or several fluorescent molecules are added, plus some additives for special applications. Thus, each component of the material can be modified (polymer [5], primary [6] and secondary fluorophores [7], and dopants [8]) as long as they respect the fundamentals in scintillation counting and photo-physics. The photo-physical interactions occurring in these materials respect Förster theory [9] and are described in Figure 1.

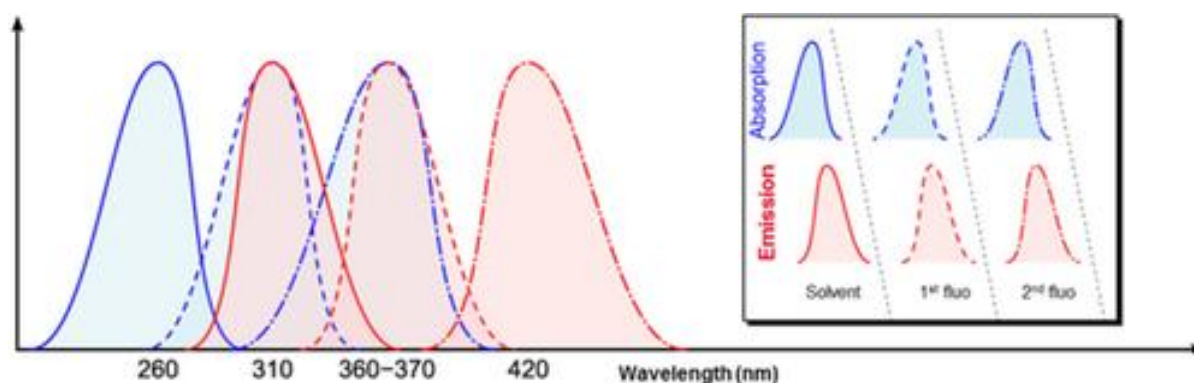


Figure 1. Schematic representation of Förster theory as typically applied for liquid or plastic scintillators.

To the best of our knowledge, the carbazole moiety has not found much success in scintillation applications. Early work from Kallmann [10], Sangster and Irvine Jr. [11] describes the use of the carbazole pattern as a primary fluorophore in a liquid scintillator or in the single crystal state, respectively. Poly(*N*-vinylcarbazole) (PVK) has shown interesting features and will be fully described in the following section. Recently, we showed the first-time use of a carbazole derivative, namely *N*-(2-ethylhexyl)carbazole (hereafter abbreviated as EHCz), as a liquid scintillator [12]. Based on the excimer emission of the molecule, it can act as a whole-liquid scintillator without addition of any further compound.

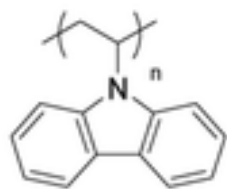
Mainstream plastic scintillators are composed of a matrix, a primary and a secondary emitter, and this study investigates the application of a carbazole derivative as each of these components. In fact, it is still surprising that this molecule has not been used frequently in this field, since the carbazole moiety is both versatile and efficient enough to be added as a fluorescent probe with different roles, namely:

1. As the matrix, for example in the form of PVK or as a copolymer with another suitable monomer;
2. As a first fluorophore, with the simplest molecule being carbazole, or a carbazole with various substitutions for example, at the *N* position;
3. As the secondary fluorophore.

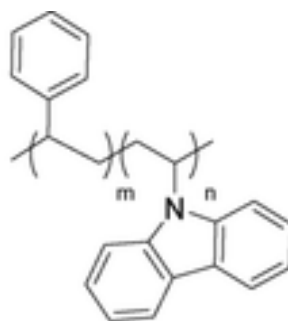
This work presents the incorporation of the carbazole moiety in a plastic matrix and its evaluation for the design of new plastic scintillators, where the carbazole moiety takes the role of one of the above mentioned three components. As a proof of concept, several carbazole derivatives were evaluated in various plastic scintillator formulations (Figure 2). Polyvinylcarbazole and poly(*N*-vinylcarbazole-*co*-styrene) were first employed as the matrix. Next, as the primary fluorophore *N*-(2-ethylhexyl)carbazole (EHCz) and a parent, solid molecule, namely *N*-ethylcarbazole (EtCz) were investigated. Finally, 2,4,5,6-

tetrakis(carbazol-9-yl)-1,3-dicyanobenzene (4CzIPN) was used as a potent secondary fluorophore.

Carbazole in the polymer

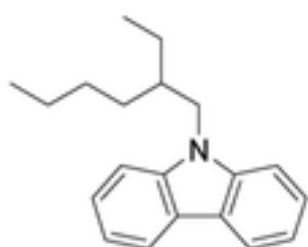


PVK

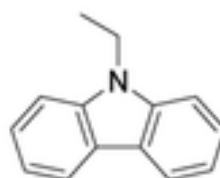


PS-co-PVK

Carbazole as the primary fluorophore

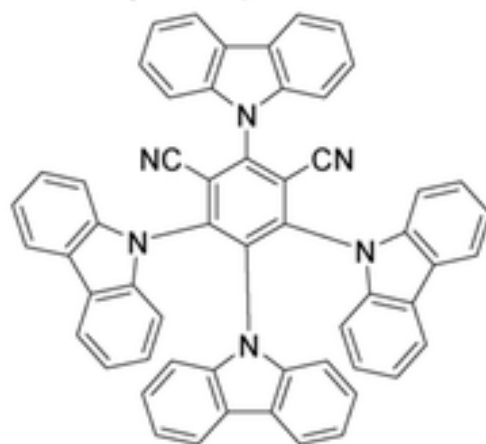


EHCz



EtCz

Carbazole as the secondary fluorophore



4CzIPN

Figure 2. Different carbazole derivatives employed herein as the matrix, primary and/or secondary fluorophore components.

The photo-physical properties of these materials were then investigated by means of absorption and emission spectroscopy and fluorescence decay lifetime measurements (using time correlated single photon counting (TCSPC) or time-resolved emission spectroscopy (TRES)). Once incorporated in a plastic scintillator, the behaviour of each system under ionizing radiation was checked by using beta or gamma sources. The results show that chemical modification leads to important improvements for the materials obtained with scintillators based on regular carbazole derivatives. When EHCz was employed, a high

concentration loading led to scintillators with better light yield resulting from the excimer emission of the fluorophore.

2 Results and Discussion

As outlined in the Introduction, we set out to investigate the application of carbazole derivatives in the polymer matrix or as the primary or secondary fluorophores. We first focused on the simplest system containing the highest composition of carbazole, namely PVK.

2.1 Direct Incorporation of Carbazole in the Matrix

To give an efficient liquid scintillator, we have previously reported that EHCz can act as the sole molecule, leading to monomolecular liquid scintillators with an emission wavelength close to $\lambda=420$ nm and a scintillation yield close to 7200 ph MeV⁻¹ [12]. To design a plastic scintillator bearing the carbazole moiety in the polymer matrix, the first approach is to perform the bulk polymerization of *N*-vinylcarbazole. There have been only a few reports of the use of this molecule for scintillation applications, mainly due to the fact that its polymerization is tricky when attempting to obtain large volumes. To the best of our knowledge, only a single report refers to the preparation of a relatively large, 48 cm³ sized PVK scintillator [13]. Usually, only 1 cm³ sized materials are described [14]. We would consider that this is probably why currently no commercial supplier offers PVK-based plastic scintillators. Our own production process led to the development of a 12 cm³, unloaded PVK material. The scintillation characteristics of the materials were obtained, with our interest focusing on the PVK material itself.

PVK was found to display a radioluminescence centred at 425 nm, with an estimated light yield of 2000 ph MeV⁻¹, relative to an EJ-200 plastic scintillator of the same volume and with the same setup experiment (see the Experimental Section for a full description). The reported photoluminescence decay of PVK is 42 ns [15]. It indicates a long-order absorption–emission process, since the decay time of diluted carbazole in toluene when excited at 274 nm is only 11 ns. When compared to other aromatic polymers, which can be used as potent matrices for plastic scintillation, that is, without any fluorescent additives, PVK displays reasonably good physical properties. However, harsh and costly processing may preclude its use from future application, such as radiation portal monitors where big volumes such as 10 L or more are necessary.

To incorporate carbazole in the polymer matrix, another possibility is to mix PVK into a polystyrene (PS) matrix. A poly(*N*-vinylcarbazole-*co*-styrene) material containing 1,4-bis(5-phenyloxazol-2-yl) (POPOP) has already been reported and used as a plastic scintillator [16]. Presumably, this system may behave as a regular scintillator, where the carbazole-containing polymer plays the role of polymerized primary fluorophore and POPOP is the wavelength shifter. Despite all our efforts, attempts to prepare unloaded poly(*N*-vinylcarbazole-*co*-styrene) led to samples with high turbidity due to the large difference of refractive indexes between PVK and PS (1.68 and 1.59, respectively).

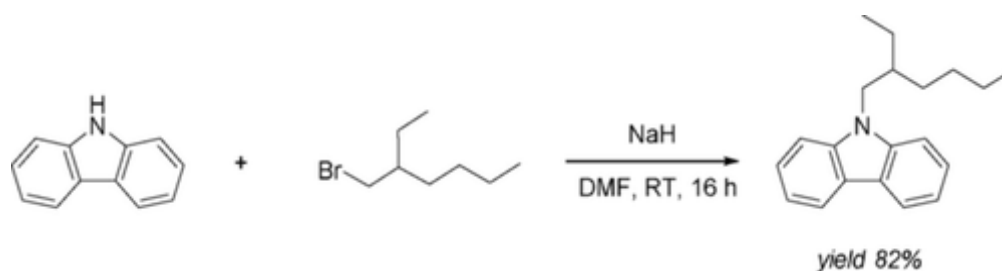
2.2 Carbazole Derivatives as the Primary Fluorophore

We next turned our attention towards the application of the carbazole moiety as the primary or secondary fluorophore. Two different molecules were investigated. First, *N*-(2-ethylhexyl)carbazole (EHCz) with a concentration range 1–40 wt % was incorporated into a specially designed cross-linked polystyrene matrix. When the concentration of EHCz is

increased, various emitting species come into play. The monomer emission has the characteristics of a primary fluorophore (with $\lambda_{em} \approx 370$ nm), whereas the excimer emission allows the system to respond as a dual primary + secondary fluorophore ($\lambda_{em} \approx 400$ nm). The second molecule evaluated as a primary fluorophore was *N*-ethylcarbazole (EtCz), a nonpolymerizable equivalent of *N*-vinylcarbazole. This molecule was embedded in the same matrix at regular concentrations (i.e. ≤ 3.5 wt %). The full list of the samples prepared with EHCz or EtCz in this study is given in Table 1. The preparation of EHCz is described in Scheme 1.

Sample	First Fluorophore (Concentration) [wt %]	Second Fluorophore (Concentration) [wt %]
1	EHCz (1)	-
2	EHCz (2)	-
3	EHCz (3)	-
4	EHCz (4)	-
5	EHCz (5)	-
6	EHCz (3)	POPOP (0.03)
7	EHCz (3)	Bis-MSB (0.03)
8	EHCz (10)	-
9	EHCz (20)	-
10	EHCz (30)	-
11	EHCz (40)	-
12	EtCz (0.7)	-
13	EtCz (1.4)	-
14	EtCz (2.1)	-
15	EtCz (2.8)	-
16	EtCz (3.5)	-

Table 1. Composition of the EHCz or EtCz plastic scintillators employed in this work.



Scheme 1. Synthesis of *N*-(2-ethylhexyl)carbazole.

The steady-state fluorescence of all samples is reported in Figure 3. All scintillators with EHCz concentration below 20 wt % show an emission spectrum centred around $\lambda = 368$ nm, in total agreement with the diluted dye emission in the liquid state [12]. For higher concentrations such as 30 and 40 wt %, the excimer of EHCz starts to luminesce together with its monomeric form, thereby shifting the overall response of the material towards 400 nm. The photoluminescence maxima of the various samples are reported in Table 2. This remarkable effect is of particular interest since the emission is now being shifted to the region where the sample is transparent to its own light, thus reducing self-absorption. Between $\lambda = 400$ and 500 nm, the samples exhibit a relatively high transmittance, starting from 22 % at 400 nm and reaching 80 % at 500 nm. In other words, when increasing the EHCz concentration from 1 to 40 wt %, there is a cut-off of the absorption spectra (given at absorption 1.5, giving ≈ 3 % of light transmission) which shifts from 370 nm (at low concentration) up to 410 nm (at

high concentration). As expected, incorporating a secondary fluorophore such as POPOP or bis-(2-methylstyryl)benzene (bis-MSB) in plastic scintillators **6** and **7** adds an extra absorption band in the $\lambda = 375\text{--}400$ nm region, along with the regular absorption band of EHCz. As a result, the emission wavelength maximum is the one of POPOP and bis-MSB, located thus around 420 and 424 nm, respectively.

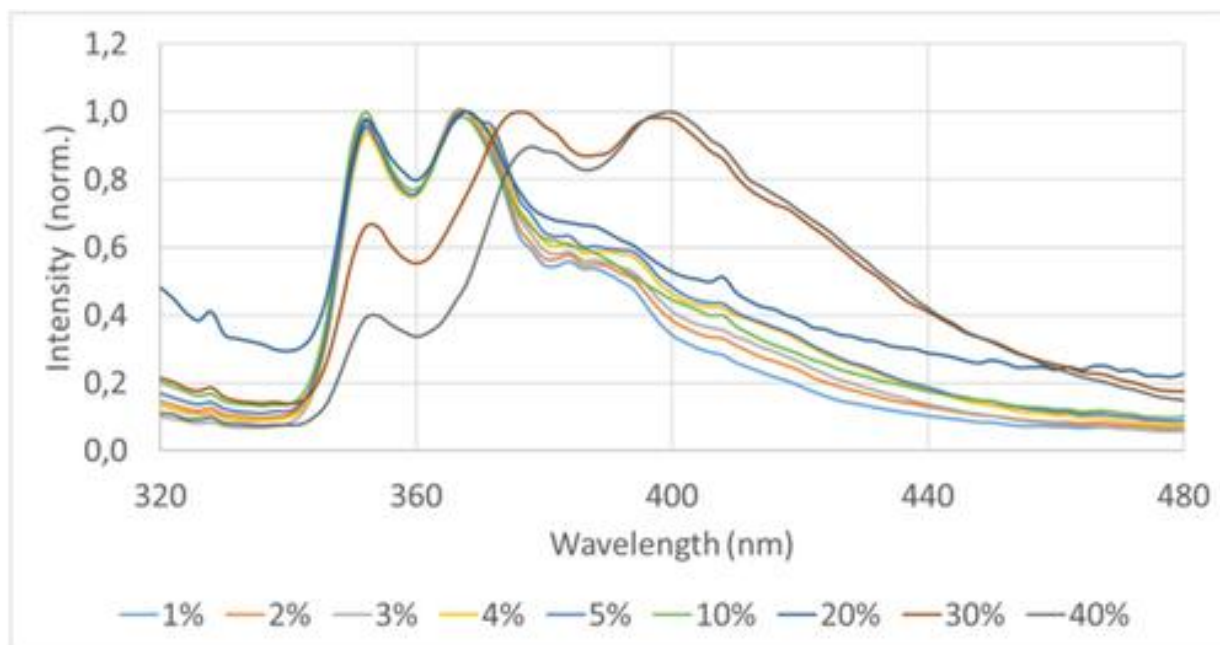


Figure 3. Steady-state fluorescence spectra of samples **1–5** and **8–11** ($\lambda_{\text{ex}} = 300$ nm). The percentage given in the caption is the EHCz content in each scintillator.

Sample	EHCz [wt %]	$\lambda_{\text{em}}^{\text{max}}$ [nm] ^[a]	$\lambda_{\text{radiolum}}^{\text{max}}$ [nm] ^[a]	τ [ns] ^[b]	Quantum efficiency [%]
1	1	366	394	14.9	24.9
2	2	368	396	15.1	24.8
3	3	368	396	15.0	24.9
4	4	368	394	15.8	24.8
5	5	368	396	15.8	24.8
8	10	368	412	13.5	24.8
9	20	368	416	14.4	24.3
10	30	376	416	19.1	24.6
11	40	400	424	22.1	24.6

[a] ± 1 nm.

[b] The photoluminescence decay time τ is given as the mean value $I(t)$, calculated according to Equation (1). It has been recorded at 370 nm for samples **1–5** and **8**, and at 410 nm for samples **9–11**, with a 274 nm excitation wavelength for all samples.

Table 2. Photoluminescence and radioluminescence maxima, decay time of the samples **1–5** and **8–11**, and quantum efficiencies of the EHCz plastic scintillator–photocathode couples.

The radioluminescence was also recorded for samples **1–11**, and the main results are given Table 2. One can notice the shift between the photoluminescence and the radioluminescence maxima, with a $\Delta\lambda$ value in the range 24–30 nm (more red-shifted for the radioluminescence). However, all of the scintillators display the same trend as in the photoluminescence values, which is the increase of the emission wavelength with the concentration. This shift can be

attributed to several factors: Although the fluorescence is recorded with a front-face excitation, the SrY source excites the material opposite to the emission chamber. Therefore, the self-absorption might affect the global response of the scintillator. Due to the low intensity of the scintillation, the emission slit is wide open.

For dual emission fluorescence, the decay time (τ) corresponds to following equation [Eq. 1]:

$$I(t) = A_{fast}e^{-t/\tau_{fast}} + A_{slow}e^{-t/\tau_{slow}} \quad (1)$$

In our case the fast decay time corresponds to the emission of the EHCz monomer. To record this, sample **1** was excited with a 274 nm pulsed LED. With an emission wavelength of 370 nm, the observed decay time was almost mono-exponential with a value of 14.9 ns. This lifetime value is moderately fast compared with regular compositions [17] and is slightly higher than the one measured in solution for the same molecule diluted at 10^{-2} m in dichloromethane (10.2 ns) [12]. When the scintillator contains more EHCz, the resulting fluorescence spectra might be the convolution of both monomer and excimer EHCz emissions (Figure 3). This effect becomes particularly visible for sample **9**, which is a 20 wt % loading of EHCz.

To determine the dynamic evolution of the global photoluminescence decay, time-resolved emission spectroscopy (TRES) was used. Samples were excited at a wavelength of 274 nm and the emission was recorded in the range $\lambda = 360\text{--}550$ nm. The results are presented in Figure 4. As expected, it clearly shows the red shift of the emission when increasing the EHCz concentration in the plastic scintillator, as well as the increase of the decay time value. The mean value $I(t)$ is reported in Table 2.

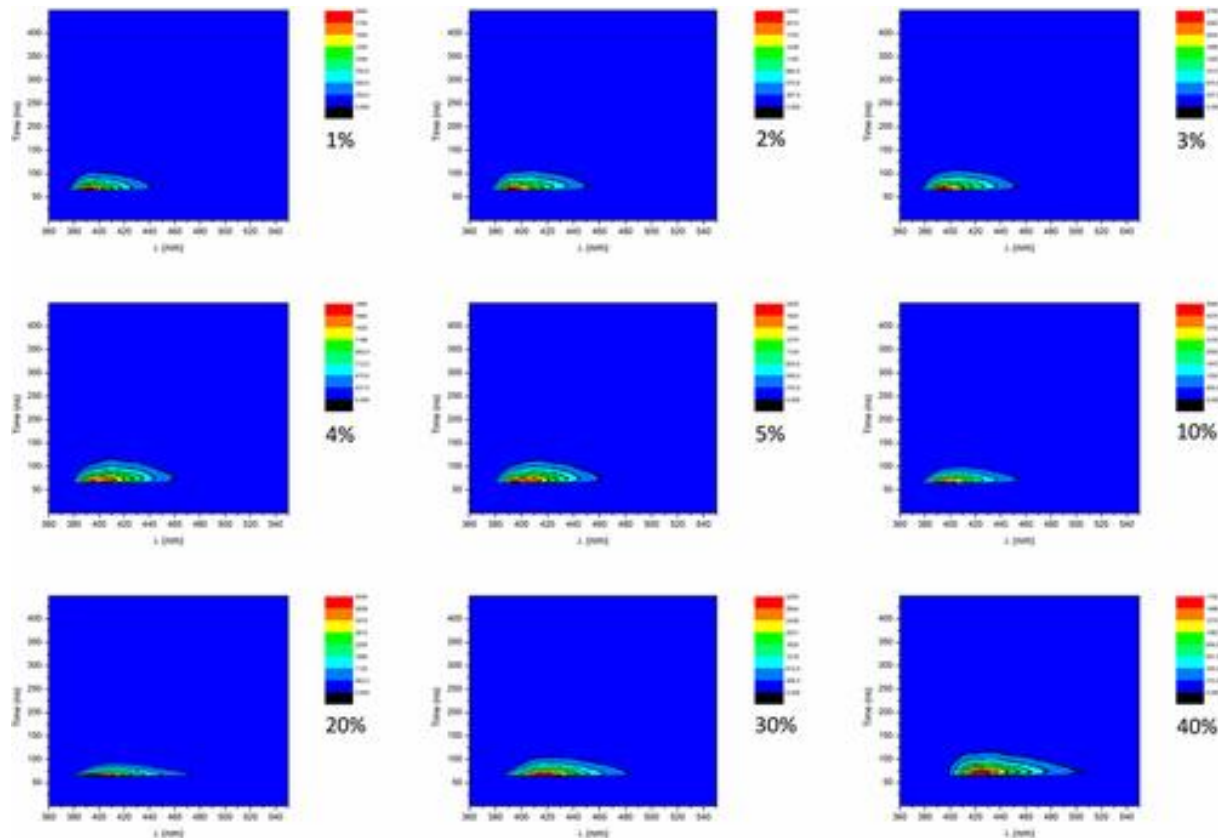


Figure 4. Time-resolved emission spectroscopy of plastic scintillators **1–5** and **8–11** loaded with 1 to 40 wt % of EHCz.

We also investigated whether or not any of the prepared scintillators could phosphoresce. However, after measuring the photoluminescence spectra 40 μ s after the excitation pulse, no phosphorescence was detected for samples **1** and **11** (1 wt % and 40 wt %, respectively), nor for a reference standard plastic scintillator.

Next, the scintillation performances of our samples were evaluated. Energy spectra were recorded using a ^{60}Co radioactive source impinging the scintillator, which was coupled to a Hamamatsu H1949-51 photomultiplier tube (PMT). A lab-made electronic board was used to digitize all the waveforms. For each scintillator, the position of the Compton edges was evaluated as a key to a relative light yield. The results presented in Figure 5 show that the light emitted by the scintillator is not very bright at low concentrations, but this value increases for concentrations up to 4 wt %. In the range 5 to 10 wt % the light decreases, probably due to self-absorption quenching of the molecule. Then the excimer form of EHCz starts to luminesce for the samples with high EHCz concentrations (**10** and **11**), therefore shifting the overall emission to longer wavelengths, which is more suitable for the H1949-51 PMT used in this experiment. This trend is in complete agreement with the emission spectra shown in Figure 3. Therefore, the scintillator is detected as more luminous by the PMT as a result of the excimer form of EHCz which allows the fluorescence in the transparent wavelength domain of the scintillator. Interestingly, the calculation of the quantum efficiency of the scintillator–photocathode couple showed a relative constancy, with values evolving in the range 24.3–24.9 % (Table 2). This quantum efficiency is based on the area normalization of the fluorescence spectrum, meaning that intrinsically EHCz excimers lead to more efficient scintillators than molecular EHCz.

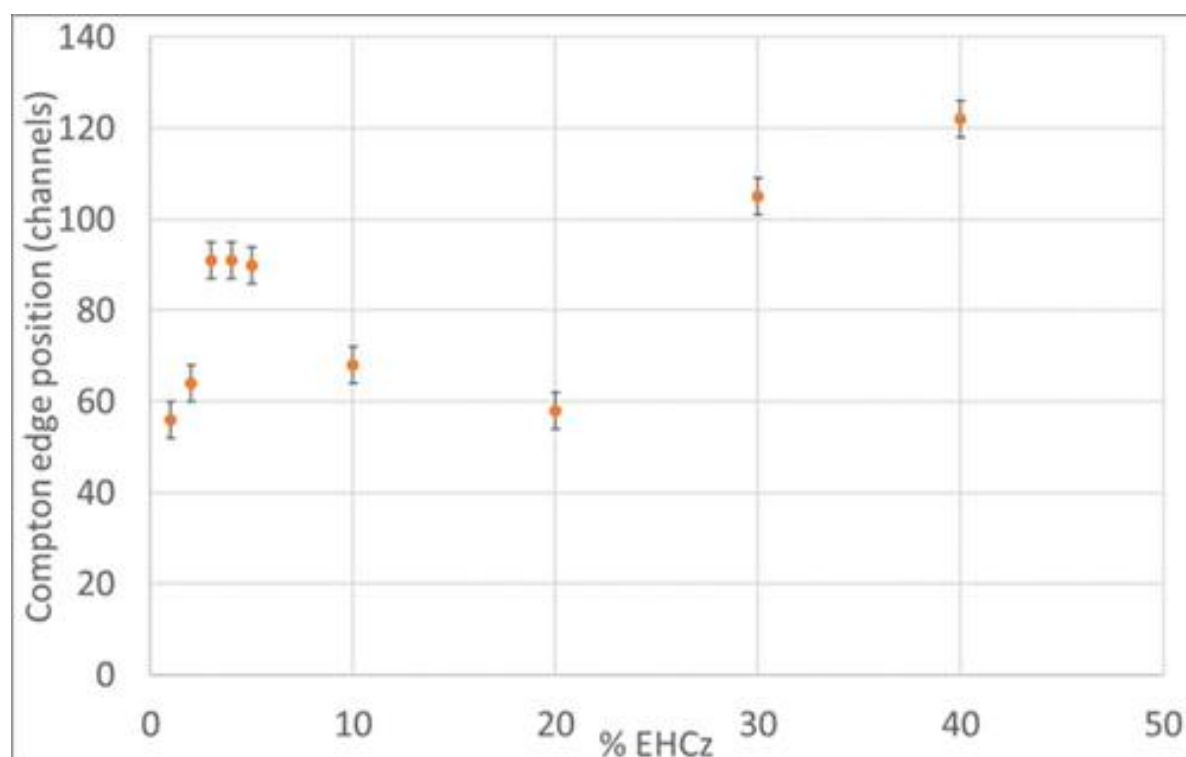


Figure 5. Evolution of the Compton edge position with the EHCz content in the polystyrene matrix (samples **1–5**, **8–11**), when exposed to a 387 kBq ^{60}Co source. Error bars are given relative to the estimation of the CE position (± 4 channels).

When EHCz was used as a regular primary fluorophore, that is, coupled with wavelength shifters such as POPOP or bis-MSB, an expected beneficial effect in the scintillation properties was observed. Four samples were exposed to a gamma-emitting source: One composed of 3 wt% of EHCz in a modified polystyrene, two others with the same composition plus bis-MSB or POPOP at low concentrations (samples **3**, **6** and **7**, respectively), and an EJ-200 commercial sample of approximately the same size and volume. Assuming the EJ-200 light yield as 10 000 ph MeV⁻¹, samples **3**, **6** and **7** have relative light yields equal to 2000, 4400, and 7000 ph MeV⁻¹, respectively. Once again, their fluorescence spectra reveal only the fluorescence of the secondary fluorophore, even when the excitation light is performed in the absorption region of the polystyrene matrix, thus revealing an efficient energy transfer. In this way, we can estimate a scintillation yield for all samples (values reported in Table 3).

Sample	EHCz [wt %]	Relative scintillation yield [ph MeV ⁻¹]
1	1	1230
2	2	1400
3	3	2000
4	4	2000
5	5	1980
6	3 + POPOP	4400
7	3 + bis-MSB	7000
8	10	1500
9	20	1280
10	30	2300
11	40	2700

Table 3. Relative scintillation yield of samples **1–11**, set as 10 000 ph MeV⁻¹ for an EJ-200 plastic scintillator of the same volume.

To compare the scintillators based on EHCz with those containing EtCz, a beta-particle-emitting radioactive source, namely ³⁶Cl was used (activity 6 kBq). This isotope is a pure beta emitter, with an average energy of 251 keV, allowing therefore the full release of its energy in the first millimetre of the plastic scintillator. Therefore, the resulting signal takes into account the overall self-absorption of the material. Thus, samples containing 1–5 wt% of the carbazole derivative were prepared and tested (samples **1–5** and **12–16**), and for better comparison the fluorophores were loaded at the same molarity. The materials were compared in terms of relative scintillation yield and the results are shown in Figure 6. Based on the position of the full energy absorption band of the ³⁶Cl radioactive source, EHCz-based plastic scintillators are almost twice as luminous as the EtCz-based materials.

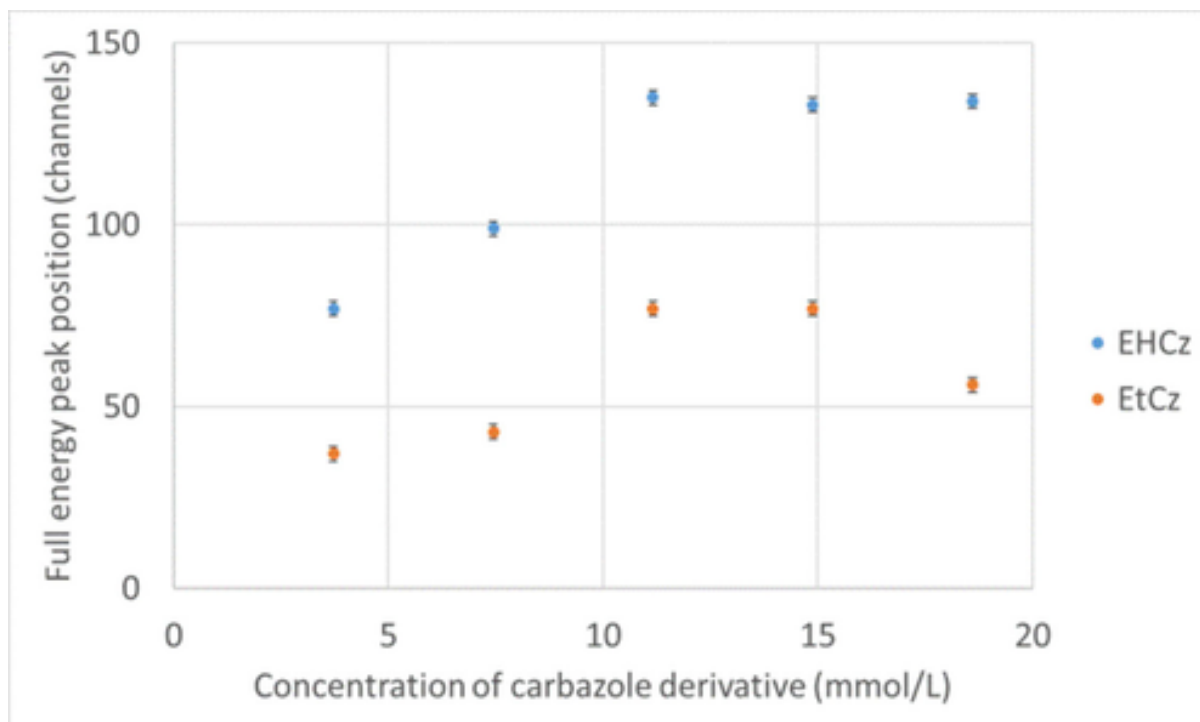


Figure 6. Evolution of the relative light yield of plastic scintillators containing various concentrations of EHCz (in blue, samples **1–5**) and EtCz (in orange, samples **12–16**), when exposed to a 4π , 6 kBq ^{36}Cl source. Error bars are given relative to the estimation of the full energy peak (± 2 channels).

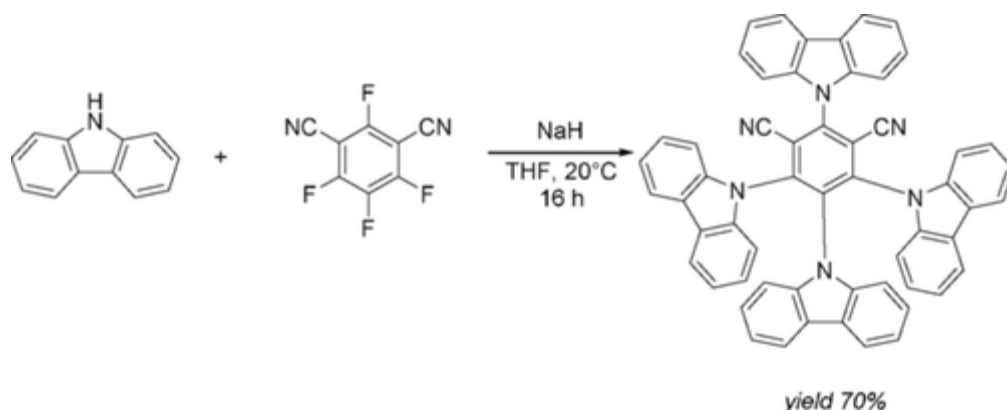
It is noteworthy that the behaviour between the samples **1–5** follows the same trend as in Figure 5, but with a less pronounced difference between samples **3** to **5**, whose response is almost identical when exposed to electrons. The better response of the highly-loaded materials with exposure to gamma rays can be partially explained by the fact that gamma particles irradiate the whole volume of the material whereas beta particles are limited to excitation of the material contained only within the first millimetre, which enhances self-absorption.

These results indicate that the carbazole moiety is a promising candidate as a very efficient primary fluorophore for scintillation applications. However, careful choice of carbazole derivative is crucial to success of the material as a scintillator, as demonstrated by the differences in performance between EHCz and EtCz. An additional benefit of carbazole as a scintillation material is that excimer formation is possible, thereby shifting the emission wavelength far away from self-absorption, albeit with a moderate light yield.

2.3 Carbazole Derivative as the Secondary Fluorophore: 4CzIPN

4CzIPN has found many applications in the field of OLEDs [18], and it was also reported in the field of plastic scintillation as a potent molecule able to perform thermally activated delayed fluorescence (TADF) [19]. The product was obtained in a single step by SN_{Ar} reaction starting from previously deprotonated carbazole with sodium hydride and 2,4,5,6-tetrafluoroisophthalonitrile in THF at room temperature (Scheme 2). 4CzIPN was added at low concentration into styrene, in addition to the other primary fluorophores. The plastic scintillators obtained after heating and their corresponding compositions are described in Table 4. Some materials even contained two carbazole derivatives such as EHCz and 4CzIPN (samples **20–24**). Fluorescence spectra of the samples reveal an efficient transfer to the

wavelength-shifter, since no emission from the primary fluorophore remained visible, and the emission wavelength was thus centred in the range $\lambda = 500\text{--}504\text{ nm}$.



Scheme 2. Synthesis of 4CzIPN [18].

Sample	First fluorophore (Concentration) [wt %]	4CzIPN [wt %]	β light yield [%] ^[a]
17	PPO (3)	0.03	98.6
18	PPO (3)	0.076	49.3
19	<i>p</i> -terphenyl (1.5)	0.03	62.0
20	EHCz (1)	0.03	70.4
21	EHCz (2)	0.03	87.3
22	EHCz (3)	0.03	87.3
23	EHCz (4)	0.03	94.4
24	EHCz (5)	0.03	100.0

[a] Relative to 100 for the best sample, based on the full energy peak position.

Table 4. 4CzIPN plastic scintillators composition list and their relative beta light yield.

The different materials **17–24** were then exposed to ionizing radiation. The emission wavelength of 4CzIPN is not particularly suited for regular photomultiplier tubes whose maximum of efficiency is centred around 420 nm. However, green-enhanced PMTs exist, so an ET9954B PMT was chosen to evaluate the scintillation performances [20]. With the exception of the substitution of the PMT, the same experimental setup was used to determine the relative light yield of samples **17–24**. Again, a ^{36}Cl , beta-particle-emitting radioactive source was chosen to better evaluate the materials for scintillation purposes. Energy spectra were recorded and the comparison of the full energy peak position is shown in the Table 4. Unfortunately no commercial sample was available to evaluate a relative scintillation yield. From these results one can see the good scintillation behaviour of the samples. Sample **18**, which contains twice the 4CzIPN quantity of sample **17**, was probably too concentrated, since the beta-particle light yield dramatically decreased, possibly indicating an increase of the self-absorption. A 2,5-diphenyloxazole (PPO)-based material displayed a better light yield than the *p*-terphenyl-based plastic scintillator (samples **17** and **19**, respectively). A reliable trend was observed for the fully carbazole derivative loaded plastic scintillators (EHCZ at various concentrations + 4CzIPN, samples **20–24**), as the beta light yield increased with the EHCz concentration, indicating a better photophysical process between the primary and secondary emitters.

3 Conclusions

As the fight against terrorism has never been so important, there is a real need for efficient yet cheap radiation detectors. After having previously demonstrated the potential of *N*-(2-ethylhexyl)carbazole as a liquid scintillator, the purpose of this work was to unveil that more globally, the carbazole framework is suitable for organic scintillation. Despite the fact that PVK scintillators are difficult to prepare according to the scintillation specification sheet, EHCz is a good candidate as a primary fluorophore. When added at low concentration, it can be considered as a regular primary emitter, such as PPO or *p*-terphenyl, and must therefore be used in synergy with a wavelength-shifter such as POPOP. The main drawback is the high price of commercial EHCz, which is around 50 times that of PPO (\approx € 1 per gram from Sigma–Aldrich). However, we have seen herein a reliable and high-scale preparation which counteracts this limitation. Starting from carbazole and 2-ethylhexylbromide, it is possible to synthesize EHCz at a competitive price of € 2 per gram.

When EHCz is added at very high concentration, typically more than 20 wt %, its excimer form becomes predominant and suitable for scintillation counting. As a result of its liquid form, and unlike most carbazole derivatives which are solid, it can homogeneously be added at very high content into a polystyrene matrix. Thus, the as-prepared plastic scintillators display moderate to good scintillation characteristics, with observed relative light yields in the range 1200–7000 ph MeV⁻¹. Another carbazole derivative was also reported and integrated in a polystyrene matrix, namely 4CzIPN. Preliminary results show once again good scintillation properties, mostly for the dual-carbazole-containing scintillator **24** with its beta light yield slightly higher than the PPO/4CzIPN formulation.

Experimental Section

General Considerations

Solvents were purchased from Carlo Erba and degassed prior to use by bubbling argon gas directly into the solvent. Monomers were distilled over CaH₂ under reduced pressure to get rid of inhibitors and impurities. *N*-ethylcarbazole, styrene, cross-linkers, calcium hydride, sodium hydride and 2-ethylhexylbromide were obtained from Sigma–Aldrich. Carbazole was purchased from Labosi or from Sigma–Aldrich. 2,4,5,6-tetrafluoroisophthalonitrile was obtained from TCI Europe.

¹H and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz respectively on a Bruker AVANCE 400 spectrometer. Chemical shifts (δ) are given in ppm, referenced to the residual proton resonance of CHCl₃ (7.26 ppm). Coupling constants (*J*) are given in Hertz (Hz). The terms m, s, d, t and sept, refer to multiplet, singlet, doublet, triplet and septuplet.

EHCz was synthesized according to a previously published procedure [12]. Carbazole (4.00 g, 23.9 mmol, 1 equiv) and NaH (1.32 g, 55 mmol, 2.3 equiv; previously washed with pentane to remove mineral oil) were stirred under argon in DMF (100 mL) for 30 min. 2-Ethylhexylbromide (5.2 mL, 29.3 mmol, 1.2 equiv) was added dropwise and the mixture was stirred overnight. Water (50 mL) was added and the product was extracted with diethyl ether (3×100 mL). The combined organic layers were concentrated to 50 mL and washed with brine (3×50 mL). The organic phase was dried with anhydrous magnesium sulfate, filtered and concentrated to dryness. The product was purified by column chromatography (SiO₂; cyclohexane) to afford a colourless oil (5.5 g, 19.7 mmol, 82 %; Lit. [21] 49 %). ¹H NMR (CDCl₃, 400 MHz): δ =0.86 (t, 3 H, ³*J*=7.3); 0.91 (t, 3 H, ³*J*=7.3); 1.21–1.43 (m, 8 H); 2.07

(sept, 1 H, $^3J=6.7$); 4.10–4.21 (m, 2 H); 7.39 (d, 4 H, $^3J=8.2$); 7.45 ppm (dt, 4 H, $^3J=6.9$, $^4J=1.1$).

4CzIPN was prepared according to another procedure [18]. Carbazole (1.67 g, 10 mmol, 5 equiv) and 60 % NaH in mineral oil (0.48 g, 12 mmol, 6 equiv) were covered by dry THF (40 mL) under an argon atmosphere. The mixture was stirred at room temperature for 30 min. 2,4,5,6-tetrafluoroisophthalonitrile (400 mg, 2 mmol, 1 equiv) was added to the mixture which turned instantaneously to yellow/orange. The solution was stirred overnight at room temperature. THF was evaporated to dryness and the residue was purified by column chromatography (SiO₂; CH₂Cl₂/cyclohexane 2:1 v/v) to afford a yellow powder (1.10 g, 1.4 mmol, 70 %; Lit. [18] 38 %). ¹H NMR (CDCl₃, 400 MHz): $\delta=6.63$ (dd, 2 H, $^3J=7.4$); 6.82 (dd, 2 H, $^3J=7.4$); 6.84 (d, 2 H, $^3J=8.0$), 7.09 (m, 8 H); 7.22 (dd, 2 H, $^3J=7.2$); 7.22 (d 2 H, $^3J=6.0$); 7.33 (d, 2 H, $^3J=7.6$); 7.49 (dd, 2 H, $^3J=7.2$, $^4J=1.6$); 7.70 (m, 8 H); 8.22 ppm (d, 2H $^3J=7.6$). ¹³C NMR (CDCl₃, 100 MHz): $\delta=109.3$ (2 C–H); 109.4 (2 C–H); 109.9 (4 C–H); 111.6 (2 C_{quat}); 116.2 (2C, C \equiv N); 119.6 (2 C–H); 120.4 (4 C–H); 120.9 (2 C–H); 121.3 (2 C–H); 121.9 (4 C–H); 122.3 (2 C–H); 123.8 (4 C_{quat}); 124.4 (2 C_{quat}); 124.7 (2 C–H); 124.9 (2 C_{quat}); 125.7 (4 C–H); 126.9 (2 C–H); 134.6 (2 C_{quat}); 136.9 (2 C_{quat}); 138.1 (4 C_{quat}); 139.9 (1 C_{quat}); 144.5 (1 C_{quat}); 145.1 ppm (2 C_{quat}).

General Procedure for Plastic Scintillator Preparation

The preparation of the cross-linked polystyrene materials has been patented [22]. Desired fluorophores and monomers were placed in a suitable round-bottom flask. The mixture was put under a nitrogen atmosphere and then frozen using liquid nitrogen and several freeze–pump–thaw cycles were performed to achieve total degassing. The resulting solution was poured into a cylindrical glass for the polymerization process. When total polymerization was observed, the mold was cooled down at room temperature and then shattered to free the plastic piece. The cylindrical samples were shaped, polished and covered either with a reflecting paint or Teflon[®] for the scintillation experiment. Poly(*N*-vinylcarbazole-*co*-styrene) was prepared accordingly to this procedure.

Poly(*N*-vinylcarbazole)-based scintillators were prepared as follows. Previously sublimed *N*-vinylcarbazole was added into a mold. It was heated at 65 °C under nitrogen atmosphere for 4 days. After complete polymerization, the scintillator was allowed to reach room temperature over 24 h. The mold was broken to liberate the bulk material which was cut, polished and covered with Teflon[®].

Photophysics

UV/Vis absorption spectra were measured at room temperature on a Jenway 6715 UV/Vis spectrometer.

Fluorescence, radioluminescence time-resolved emission spectroscopy (TRES) and time-correlated single-photon-counting (TCSPC) experiments were performed with a Horiba Jobin Yvon Fluoromax 4P spectrofluorometer, operated with FluorEssence or Datastation softwares. Radioluminescence spectra consisted of recording the photoluminescence spectrum (intensity as a function of the wavelength). They were acquired by using the following procedure: in the Fluoromax 4P spectrofluorometer, the excitation light was shut down. In the centre of the experimenter chamber, a ⁹⁰Sr–⁹⁰Y β -emitting source (37 MBq) was placed close to the scintillator cell, opposite to the emission chamber. Beta particles are deposited into one face of the scintillator, which provokes the photoluminescence of the entire material. Spectra were acquired with an integration time of 0.1 s nm⁻¹, and adjustable slits to give ca. 10 000 counts at the maximum of the signal. TRES and TCSPC experiments were performed by

illuminating the plastic scintillator with a laser diode operating at 274 nm. Fitting of the fluorescence decays was achieved with Horiba Jobin Yvon DAS6 software.

Scintillation Experiments

An EJ-200 plastic scintillator was obtained from Eljen technology. It was cut and polished in our own facility.

Gamma spectra were recorded as follows: Samples emitting in the violet to blue region were optically coupled to a Hamamatsu H1949-51 photomultiplier tube operating at -1480 V, whereas samples emitting at 500 nm were coupled with silicon grease as well to an Electron Tube 9954B PMT operating at $+2000$ V. A 387 kBq ^{60}Co radioactive source was used to excite the material. The gamma source was located 10 cm away from the plastic scintillator. For beta experiments, a 4π , 6 kBq ^{36}Cl radioactive source was placed on the top of the plastic scintillator, allowing therefore circa 50 % of the electrons to be released inside the material. Each pulse emanating from the photomultiplier tube was digitized using a lab-made electronic board [23], which was then integrated and sorted as an energy histogram. For each experiment the background was subtracted from the energy spectrum. For gamma experiments, the method reported by Swiderski et al. was used to approximate the Compton edge position [24]. For beta experiments the top of the full energy peak was considered.

Acknowledgements

The authors thank the “Agence Nationale de la Recherche”, within the CSOSG program (ANR-12-SECU-0002), the French “Direction Générale de l’Armement” and “Secrétariat Général de la Défense et de la Sécurité Nationale” for their funding (G.H.V.B., F.S.).

Conflict of interest

The authors declare no conflict of interest.

References

- [1] G. H. V. Bertrand, M. Hamel, F. Sguerra, *Chem. Eur. J.* 2014, 20, 15660–15685.
- [2] G. H. V. Bertrand, M. Hamel, S. Normand, F. Sguerra, *Nucl. Instrum. Methods Phys. Res. Sect. A* 2015, 776, 114–128.
- [3] <http://www.eljentechnology.com/products/plastic-scintillators/ej-299-33a-ej-299-34>.
- [4] M. Hamel, F. Carrel in *New Insights on Gamma Rays*, InTech, 2017, pp. 47–66.
- [5] M. Dettmann, V. Herrig, J. Maldonis, J. Neuhaus, D. Shrestha, P. Rajbhandari, Z. Thune, M. Been, M. Martinez-Szewczyk, V. Khristenko, Y. Onel, U. Akguna, *J. Instrum.* 2017, 12, P 03017.
- [6] H. A. Yemam, A. Mahl, J. S. Tinkham, J. T. Koubek, U. Greife, A. Sellinger, *Chem. Eur. J.* 2017, 23, 8921–8931.
- [7] T. J. Hajagos, D. Kishpaugh, Q. Pei, *Nucl. Instrum. Methods Phys. Res. Sect. A* 2016, 825, 40–50.
- [8] E. S. Velmozhnaya, Y. A. Gurkalenko, D. A. Eliseev, P. N. Zhmurin, V. N. Lebedev, V. N. Pereymak, *Funct. Mater.* 2016, 23, 650–656.
- [9] T. Förster, *Ann. Phys.* 1948, 437, 55–75.
- [10] H. Kallmann, *Phys. Rev.* 1950, 78, 621–622.
- [11] R. C. Sangster, J. W. Irvine, Jr., *J. Chem. Phys.* 1956, 24, 670–715.

- [12] E. Montbarbon, F. Sguerra, G. H. V. Bertrand, É. Magnier, R. Coulon, R. B. Pansu, M. Hamel, *Chem. Eur. J.* 2016, 22, 12074–12080.
- [13] N. J. Cherepy, R. D. Sanner, T. M. Tillotson, S. A. Payne, P. R. Beck, S. Hunter, L. Ahle, P. A. Thelin, *IEEE Nucl. Sci. Symp. Med. Imaging Conf. Rec.* 2012, 1972–1973.
- [14] B. L. Rupert, N. J. Cherepy, B. W. Sturm, R. D. Sanner, S. A. Payne, *Europhys. Lett.* 2012, 97, 22002.
- [15] H. S. Nalwa, *Advanced Functional Molecules & Polymers*, Vol. 3, CRC Press, Amsterdam, 2001, p. 8.
- [16a] Z. Polacki, K. Sienicki, *Nukleonika* 1984, 29, 31–37;
- [16b] Z. Polacki, Z. Stuglik, *Nukleonika* 1986, 31, 239–247.
- [17] I. G. Britvich, V. G. Vasil'chenko, V. N. Kirichenko, S. I. Kuptsov, V. G. Lapshin, A. P. Soldatov, A. S. Solov'ev, V. I. Rykalin, S. K. Chernichenko, I. V. Shein, *Instrum. Exp. Tech.* 2002, 45, 644–654.
- [18] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* 2012, 492, 234–240.
- [19] P. R. Menge, PCT Patent Application WO2015038861, 2013.
- [20] <https://my.et-enterprises.com/pdf/9954B.pdf>.
- [21] J. Shi, M. Huang, Y. Xin, Z. Chen, Q. Gong, S. Xu, S. Cao, *Mater. Lett.* 2005, 59, 2199–2203.
- [22] M. Hamel, P. Blanc, S. Normand, C. Dehé-Pittance, French Patent Application FR3002945, 2013.
- [23] G. H. V. Bertrand, J. Dumazert, F. Sguerra, R. Coulon, G. Corre, M. Hamel, *J. Mater. Chem. C* 2015, 3, 6006–6011.
- [24] L. Swiderski, M. Moszyński, W. Czarnacki, J. Iwanowska, A. Syntfeld-Każuch, T. Szcześniak, G. Pausch, C. Plettner, K. Roemer, *Radiat. Meas.* 2010, 45, 605–607.