

University of Milan - Bicocca

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Master Degree Course in Materials Science



Scintillation Properties of Metal-Organic Framework-Based Composites for Time-of-Flight Positron Emission Tomography Imaging

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*Ho trovato più risposte
di quante domande avessi.*

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Introduction

Scintillation is a phenomenon wherein the absorption of high-energy radiation in a material leads to the emission of light from matter due to radiative recombination of excited luminescent centers. Scintillating materials are currently widely used in many detection systems addressing different fields, such as high-energy physics (HEP), homeland security, and medical imaging [1]. In the latter, the positron emission tomography (PET) technique is of significant importance for clinical oncology; the image reconstruction exploits the simultaneous detection of two back-to-back γ photons emitted following the annihilation process of a positron, originating from the injected radiotracer, with an electron of the surrounding tissue [2]. A large number of clinical studies have unequivocally demonstrated that a significant improvement concerning image quality and better signal-to-noise ratio (SNR) can be achieved by the use of the difference of the arrival times of the two annihilation photons, i.e. the time-of-flight (TOF). However, the effectiveness of this improvement is strongly correlated with the coincidence time resolution (CTR) of a detector, defined as the full-width-at-half maximum (FWHM) of the time delay distribution of arrival photons on detectors from a point source.

The CTR was recently reduced down to ~ 215 ps by Siemens Healthineers, corresponding to a spatial uncertainty of ~ 3 cm [3]. Continuous research is done every day to further improve and push it up to the intrinsic limit of ~ 1.5 mm.

To achieve such groundbreaking TOF performance, several aspects in detector development and signal processing need to be addressed. For instance, the time resolution of a scintillator is proportional to the square root of the scintillation rise and decay time but inversely proportional to the square root of the light yield ($\sqrt{\tau_r \cdot \tau_d} / LY$, as illustrated in the Hyman theory). Current scintillators based on L(Y)SO or BGO are limited on this due to its relatively long decay time of 40-300 ns and not get to the desired timing performance.

Other factors can be chemical composition, electronic structure, crystal symmetry, atomic density, and optical properties. No type of material currently used in radiation detection has the synthetic versatility to exert systematic control over these factors. Therefore, further advances in radiation detection require the development of new materials and a new approach outside the scope of traditional scintillators [4].

Metal-organic frameworks (MOFs) could potentially offer the desired level of structural control, leading to an entirely new class of radiation detection materials. They provide a tunable platform for the co-assembly of organic scintillator molecules and metal cluster nodes of high atomic numbers (Z) elements able to interact with the ionizing radiation and sensitize the ligand luminescence [5].

This Master thesis work concerns the investigation of the scintillation properties of nanocomposite scintillators based on fluorescent metal-organic-frameworks (MOF) nanocrystals designed for the TOF-PET imaging. Their framework integrates a heavy-metal (Zr) node sensitizer and an anthracene-based emitter, both embedded in polymer matrices: poly(methyl meth-acrylate) (PMMA) or poly(dimethylsiloxane) (PDMS). These materials have been prepared with different concentrations of MOFs (0.05%, 0.1%, 0.5%, and 2.5%) and characterized at the Materials Science Department (UNIMIB) to determine their photoluminescence (PL) emission spectra and PL lifetimes. The accurate investigation of their scintillation properties related to the TOF-PET imaging has been carried out in the CERN Crystal Clear laboratory in Geneva, Switzerland.

In Chapter 1 of this manuscript a discussion about scintillation, its fields of application, and its physical process is presented. Moreover, an overview of the figure of merit of scintillating materials is given.

In Chapter 2 the physical principles of PET, the main characteristic of radiation and photo-detector that are employed in PET and the PET system are discussed. A brief introduction regarding the image reconstruction approach for PET and TOF-PET is provided. Furthermore, a short discussion about TOF-PET is introduced.

In Chapter 3 the metal-organic framework-based composites that are characterized in this work are presented.

In Chapter 4 materials, method, results, and their discussion about all the experimental characterizations are given.

In Chapter 5 the main aspects which are discussed in the current work are summarized and provided the outlooks for the future.

Chapter 1

Scintillators

Firstly, an overview about scintillation and its application fields is presented, inspired by C. Dujardin [6]. The principles of the scintillation process and the figures of merit that characterize a scintillating material are then briefly described.

1.1 Introduction

Luminescence corresponds to the emission of light from matter, which can be a gas, liquid, or solid. This phenomenon occurs from the radiative recombination from an excited energy state to a less excited or relaxed state of that matter. Energy input is thus required to promote a given system into an excited state. The physical nature of this energy input specifies the luminescence type. For instance the *photoluminescence* is related to the light input, *electroluminescence* to the electric current one, and *chemiluminescence* to the chemical reaction. Instead, if an interaction between matter and ionizing radiation occurs and a light emission coming out from the system, then the process is called *scintillation*. The most commons used in the scintillating applications are X-rays, γ -rays, neutrons, protons, electrons, and α particles, however, in this work, the attention will focus on X-rays and γ -rays only.

1.2 Application fields of scintillating materials

Scintillating materials are currently widely used in many detection systems addressing different fields, such as medical imaging, homeland security, high energy physics (HEP) calorimetry, industrial control, and oil drilling exploration. Three different types of applications are given in the following sections.

1.2.1 Medical imaging

The property of X-rays to travel through opaque matter made it possible to investigate the inner parts of the body. The impact on medical diagnosis was significant and was even developed as a mobile X-ray imaging service during the First World War by Marie-Curie.

Nevertheless, this property of passing through the matter makes the absorption and thus the detection efficiency of photographic films very inconsistent. Thus, interposing a material able to absorb the X-ray and converts the deposited energy into visible light (X-ray phosphor), the sensitization of the film is obtained. Radiographic imaging has been used based on the concept of coupling an X-ray phosphor and a photographic film for some time. Nevertheless, with the progress in the fields of photodetectors and in scintillating materials, digitized imaging and even the creation of X-ray videos with a resolution of about $100\text{ }\mu\text{m}$ (depending on the conditions) has been achieved.

The second sector of the medical field is nuclear imaging such as PET. It consists of injecting activated molecules, called radiotracers, into the patient. These molecules target specific zones such as malign tumors leading to a significant cell uptake. In this case, the imaging system can detect γ -photons issuing from radioactive decay and estimate the position of the source. 3 D images of the cell containing the tracer can be produced and used for diagnosis. The commercial machine uses bismuth germanate ($\text{Bi}_3\text{Ge}_5\text{O}_{12}$) which is more and more substituted by a faster scintillator based on lutetium (-yttrium) oxyorthosilicate ($\text{Lu}_2\text{SiO}_5\text{:Ce}$) or its analog LYSO where a small fraction of lutetium is substituted by yttrium.

Scintillators may be used also in medical dosimetry. The scintillating materials optically coupled to optical fibers are emerging in vivo dosimetry during radiotherapy. The light produced by the scintillator under irradiation is supposed to be proportional to the received dose, injected into the optical fiber, and detected outside the body.

1.2.2 Homeland security

Scintillating materials are used also in homeland security. For example, airports, museums, and at borders radiographic images of luggage are widely employed. The constraints regarding acceptable doses are less critical than for a patient, indeed it enables imaging scanning various energies in order to distinguish the densities of the items contained in the luggage. It corresponds to the different colors which can be seen on the screens at the airport. For vehicles, because of the larger size and the amount of matter to pass through, more penetrating γ -rays are used.

Since the September 11 attacks in 2001, there has been significant political demand to control radioactive substance transport. Besides, the identification of the emitting elements is considered strategic from the homeland security point of view. In particular, real-time γ -ray spectroscopy is, therefore, necessary in heavily frequented places such as ports, highways, and borders.

1.2.3 High energy physics

To understand the theoretical basis of matter, particle physicists generate collisions of highly accelerated particles. These collisions lead to a massive number of secondary particles that must be detected and analyzed to reconstruct interaction scenarios. A notable fraction of these secondary particles is detected by an array of scintillators coupled with photodetectors, the hadronic and electromagnetic calorimeter. In this field, the energies involved reach the order of the TeV. It results in several tones of scintillating material used to ensure good stopping power. The high-energy particles give rise to an electromagnetic shower, consisting of a cascade of additional

particles generated through the energy loss/interaction of the first interacting particle with the matter.

1.3 Scintillation process

1.3.1 X or gamma photons interaction with matter

There are different kinds of radiation in relation to the nature of the particle that composed it. Their classification can be the following [7]:

Charged Particulate Radiations	Uncharged Radiations
Heavy charged particles Fast electrons	Neutrons X-rays and γ -rays

In this contribution, the description is restricted to the X-rays and γ -rays matter interaction.

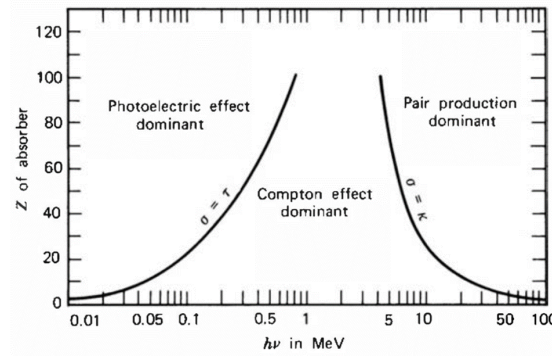


Figure 1.1 Relative importance of the three major types of γ -ray interaction. The lines show the values of Z and $h\nu$ for which the two neighboring effects are just equal (taken from [8]).

If a photon passes through matter, there is no way to predict precisely either how far it will travel before engaging in an interaction or the type of interaction it will take part in.

When a ray of photons of intensity I_0 hits a slice of material of thickness d , its attenuated intensity I can be described thank an exponential law:

$$\frac{I}{I_0} = e^{-\mu d} \quad (1.1)$$

where μ (cm^{-1}) is the *linear attenuation coefficient* and takes into account all the probabilities of possible interactions with matter μ_i :

$$\mu = \sum_i \mu_i \quad (1.2)$$

The linear attenuation coefficient depends from the intrinsic characteristics of matter according to the following formula [9]:

$$\mu = \frac{n_e \sigma_e}{Z_{eff}} \quad (1.3)$$

with Z_{eff} the effective atomic number of the material, n_e the electron density and σ the interaction cross-section per atom combining the three most dominant potential effects: the *photoelectric effect*, the *Compton effect* and the *pair creation*. The cross-section of each of these processes is a strong function of the photon energy and of the effective atomic number of the absorber medium, as shown in Fig.1.1.

Since the pair production is a threshold process it can not occur when the photon energy is less than 1022 keV (twice the electron mass). For this and for other reasons which will become clearer in the subsequent chapters, the only two interaction mechanisms which play an important role in PET are the photoelectric and the Compton effects.

Photoelectric effect

In the photoelectric effect, the absorption of an incident photon of energy E leads to ionization of one atom that constitutes the matter, since an energetic *photoelectron* is ejected from one of its bound shells. The kinetic energy of the photoelectron satisfies the energy conservation and is given by

$$E_{e^-} = E - E_b \quad (1.4)$$

where E_b represents the binding energy of the electron in its original shell. For γ -ray energies of more than a few hundred keV, the photoelectron carries off the majority of the original photon energy. Part of the electron kinetic energy is converted into light emission through a cascade of multiple interactions with matter. The ionized atom is then in an excited state with a hole in a core level. This hole recombines with a free electron from the medium or other shells of the atom. Therefore, X-ray or Auger electron can be generated and could attend at the scintillation signal. A rough approximation of the photoelectric effect probability is

$$\tau \simeq constant \frac{Z_{eff}^n}{E^{3.5}} \quad (1.5)$$

where the exponent n varies between 4 and 5 over the γ -ray energy region of interest [7]. It means that for application using the photoelectric effect the effective atomic number plays an important role and photoelectric absorption is the interaction for X-rays or γ -rays of rather low energy.

Compton effect

The interaction process involves an electron of the medium and a photon (X-ray or γ -ray photon) is called Compton effect or Compton scattering. When the photon interacts with the electron is deflected of an angle θ respect to its original trajectory. Part of the photon energy is transferred to the electron. If the electron is assumed to be initially at rest, then it gains kinetic energy E_{e^-} and is called *recoil electron*. Its energy can span from zero to large portion of the incoming

photon energy E because of the angular dependence of the process. The laws associated with the different energies are [6]:

$$E_{e^-} = E - E' \quad (1.6)$$

with E' the scattered photon energy:

$$E' = \frac{E}{1 + \frac{E}{m_0 c^2} (1 - \cos \theta)} \quad (1.7)$$

where $m_0 c^2$ is the rest-mass energy of the electron (511 keV). The transferred energy increases with the increasing of the angle θ .

The number of electrons available as scattering centers plays an important role in the dependence of the Compton cross-section σ_c , indeed it increases linearly with effective atomic number ($\sigma_c \propto Z_{eff}/E$) [9]. Moreover, considering γ -rays with energy in the range of 0.1-1 MeV, Compton scattering is the most probable interaction process (see Fig.1.1).

1.3.2 Scintillation mechanisms

The scintillators can be inorganic, organic, and hybrid materials. Their scintillation mechanisms are different and in the following paragraphs, that of inorganic and organic materials will be briefly treated.

For a matter of simplicity, the radiation matter interaction (described in paragraph 1.3.1) will be treated as an absorption process.

Scintillation mechanism in inorganic materials

In inorganic scintillators, the scintillation mechanism depends on the energy states which are determined by the crystal lattice. In pure crystals, the energy absorption leads to the promotion of an electron from the valence band (range of energy state of the electrons bounded at lattice sites) to the conduction band (range of energy state of the free electrons in the crystal) passing through the gap (range of forbidden energy state). The net result is the generation of a hole in the core bands and highly excited thus having a high kinetic energy called a hot electron. Then the electrons interact with other particles and quasi-particles, such as electrons, plasmons, excitons, phonons, defects. Each interaction leads to a multiplication process, or in other words to the creation of additional electron-hole pairs (not fully relaxed). At the end of that energy cascade, when the electron energy reaches energy below the threshold $2E_{gap}$, the electrons can only interact with phonons giving origin to the thermalization process. Holes can relax through the Auger process or with X-ray emissions. Once relaxed, all the electron-hole pairs have to be transferred to the luminescent center to recombine and emit photons. However, since electron-hole pairs interact with their environment, such as defects leading to charge traps and vibration modes of the closest neighbors, then radiativeless mechanisms can compete with the emission of photons.

Besides, band gap widths in pure crystals are such that the resulting emitted photon has a frequency too high to lie within the visible range. Therefore, to increase the probability of

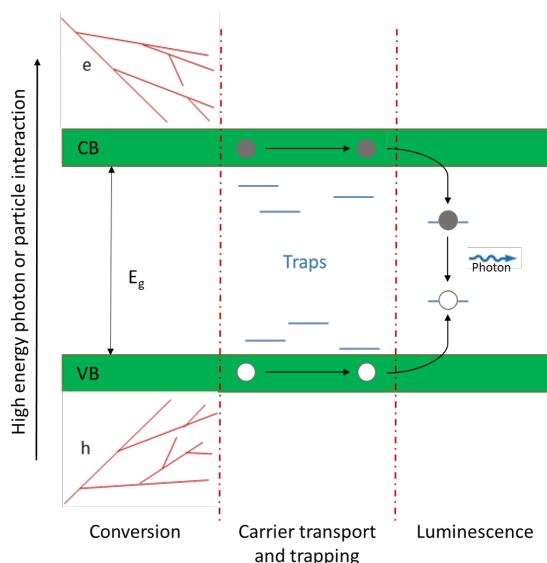


Figure 1.2 Scheme of the scintillation mechanism in an inorganic scintillator.

emitted visible photon, small amounts of impurities are thus added to the crystal and are called *activators*. They create special sites in the pure lattice and energy states within the gap. The energy structure of the overall crystal does not change, just the energy structure at the activator sites. These new states permit the de-excitation of the electrons to the valence band emitting photons in the visible range since the new energy gap is smaller than the previous. Typically, lifetimes for such excited states are of the order of 30-500 ns.

The whole mechanism is illustrated in Fig. 1.2.

Scintillation mechanism in organic materials

The fluorescence phenomenon, in organic materials case, arises from transitions in the energy levels of a single molecule and thus it can be observed independently of their physical state.

The molecules in organic scintillators have symmetry properties associated with the π -electron structure.

If a charged particle, for example, passes nearby an organic scintillator, part of its kinetic energy is absorbed and the electrons are excited from the ground state S_{00} to the upper states. The higher singlet states $S_2, S_3, \dots$, are quickly (on the order of picoseconds) de-excites to the S_1 through radiationless transitions (internal conversion). Furthermore, any state with excess vibrational energy (such as S_{11} or S_{12}) again quickly loses the vibrational energy in order to reach the thermal equilibrium with its neighbors. Therefore, after a negligibly short period, a population of excited molecules in the S_{10} state rises as the net effect of the excitation process in a simple organic crystal.

The main scintillation light is emitted in transitions between S_{10} and the ground state such as prompt fluorescence. If τ represents the fluorescence decay time for the S_{10} level, then the prompt fluorescence intensity at a time t following excitation should simply be

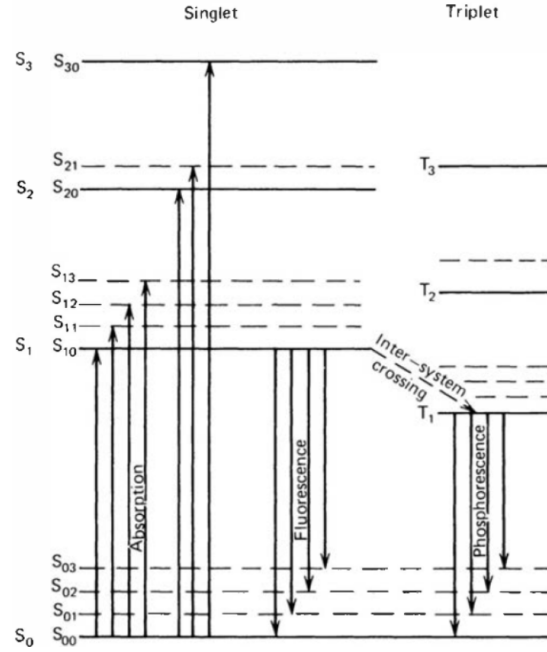


Figure 1.3 Energy levels of an organic molecule with π -electron structure (adapted from [10]).

$$I = I_0 e^{-t/\tau} \quad (1.8)$$

In most organic scintillators, τ is the order of a few nanoseconds therefore, the prompt scintillation component is fast. Because of a transition called *intersystem crossing*, some excited singlet states may be converted into triplet states. The lifetime for the first triplet state T_1 is intrinsically much longer than that of the singlet state S_1 and the radiation emitted in a de-excitation from T_1 to S_0 is, therefore, a delayed light emission also called *phosphorescence*.

The energy level scheme in Fig. 1.3 shows the mechanism explained and why organic scintillators can be transparent to their fluorescence emission. All fluorescence decays (except $S_{10} \rightarrow S_{00}$) have lower energy than the minimum required for excitation. There is little overlap between emission and absorption spectra, therefore just a little portion of the emitted light is self-absorbed [7].

1.4 Figure of merit

In this section are treated the main technical characteristics used for the description of the scintillating detectors and that they influence the whole detection chain's performance.

1.4.1 Time response

If it can be assumed that in an absorber the luminescent states are formed instantaneously and only prompt fluorescence is observed, then the time distribution of the light pulse should be a

very fast leading edge followed by a monoexponential decay (see Eq. 1.8) where the exponential time constant, called *decay time*, defines the prompt scintillation yield. A more detailed model of the time distribution of the scintillation yield has to take into account more effects as: the finite time necessary to populate the luminescent states which is described by the *rise time* (τ_r), and the multi-components associated to delayed fluorescence and phosphorescence. If it assumes that the population of the luminescent levels is also exponential, then one general describing model for the overall shape of the light pulse can be given by [11]:

$$f(t) = \Theta(t) \sum_i^N \frac{e^{-(t/\tau_{d,i})} - e^{-(t/\tau_{r,i})}}{\tau_{d,i} - \tau_{r,i}} \rho_i \quad (1.9)$$

where the function $\Theta(t)$ is the Heaviside function. The relative weights of the different components are defined by ρ_i , with $\sum_i \rho_i = 1$.

The average decay time ($\tau_{d,av}$) typically is calculated with the Eq. 1.10 is used to describe the overall decay process

$$\tau_{d,av} = \frac{\sum_i \rho_i \tau_{d,i}}{\sum_i \rho_i} \quad (1.10)$$

However, in timing applications is useful the effective decay time, which is described by a harmonic average (see Eq. 1.11 to give more importance to the fast components. This is related to the initial photon-time density (IPTD), thus it carries the information about the intrinsic timing capabilities of the scintillators [12].

$$\tau_{d,eff} = \left(\sum_i \frac{\rho_i}{\tau_{d,i}} \right)^{-1} \quad (1.11)$$

1.4.2 Density

Density is related to the absorption and attenuation of the x- and γ -ray and is a crucial parameter, as well as the effective atomic number (see paragraph 1.3). Especially, in X-ray imaging, if the material is based on a polycrystalline powder, a thicker layer leads to an enhanced diffusion of the emitted photons, which reduces the spatial resolution and sensitivity. Instead, for positron emission tomography, a larger crystal increases parallax error for zones far from the center of the field of view. Or as in high-energy physics where the energy of the particles to be detected is huge.

1.4.3 Scintillation light yield

Scintillation yield is the number of photons emitted per unit of deposited energy in the material and is expressed as number of photons per MeV (ph/MeV) or per keV (ph/keV). This figure can be also called *intrinsic light yield (ILY)*. Therefore, the scintillation yield describes the amount of kinetic energy of the ionizing radiation lost in a scintillator and converted into light. A fraction of the initial radiation energy can be dissipated due to radiativeless in form of lattice vibrations and heat.

The number of photons produced in the scintillator is not equal at that of photons detected. In fact, many light losses might be verify, such as reflections, diffusion or self-absorption. All the light losses can be summarized in the *light transfer efficiency* (*LTE*) and considering the *photon detection efficiency* (*PDE*) of the detector, the number of photons detected results to be:

$$N_{ph,det} = PDE \times LTE \times ILY \times E \quad (1.12)$$

where E corresponds to the deposited energy.

Furthermore, surface state, edge quality, and type of wrapping used for the crystal play an important role in the efficiency of light collection. Thus, maximizing the light yield not only requires selecting materials with optimal interacting properties with the radiation but also optimizing the transport of light such that the maximum photons reach the photodetector [13].

1.4.4 Energy resolution

The energy resolution (R) of a scintillator is its ability to distinguish two particles with different energies and it is defined as the ratio between the full with half maximum (FWHM) of the energy peak and the its centroid H_0 (see Fig. 1.4):

$$R = \frac{FWHM}{H_0} \quad (1.13)$$

The energy resolution may be evaluated using calibrated and monoenergetic sources (usually the 511 keV of ^{22}Na or the 662 keV of ^{137}Cs) and photodetector to collect the light coming from the scintillator. Therefore, the FWHM takes into account the inhomogeneity of the scintillator and the dispersion of light collection, and the inhomogeneity of the photodetector. Scintillation detectors used in γ -ray spectroscopy normally show an energy resolution in the range of 3-10%.

In PET sufficient good energy resolution (10-20%) is required to successfully distinguish events that scatter in the body of the patient and lose some energy, since those events would otherwise lead to a different line of response and worse SNR. For instance, 511 keV gammas which scatter at an angle of 45° have only an energy of ~ 395 keV (Eq. 1.7).

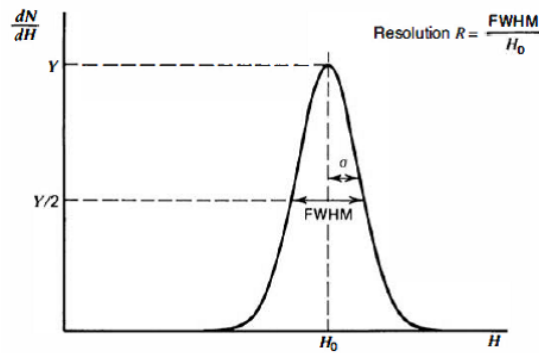


Figure 1.4 Definition of detector energy resolution (taken from [7]).

1.4.5 Emission wavelength

Fluorescent wavelength is important in photon detection in photodetector for the conversion of light in photoelectrons by the photocathode. Each detector has its spectral sensitivity. Indeed, to have a more accurate estimation of conversion efficiency, the overall emission spectrum is multiplied by the spectral sensitivity curve of the detector. For the working mechanism of two types of photodetectors see paragraph 2.3.2.

1.4.6 Radiation damage

Transmission and light losses can occur as a result of the interaction with ionizing radiation. In some cases, scintillation yield might change during irradiation. Such behavior is undesirable in imaging systems in which response linearity is expected. Crystal properties might sometimes be restored with thermal treatments up to a few hundred degrees or under light illumination, [6].

1.4.7 Chemical, thermal and mechanical stability

Besides ionizing radiation, also external factors might alter the composition of the scintillators and thus the scintillation properties. Therefore, during the research in new scintillators materials is important to test the chemical, thermal or mechanical stability exposing to those condition in which he scintillators are employed.

Chapter 2

Positron emission tomography (PET)

2.1 Introduction

Positron emission tomography (PET) is a functional imaging technique utilised in a variety of domains such as basic research in kinetic pharmaceutical studies and especially in clinical oncology. It uses a specific radioactive substance (radiotracer) to obtain a three-dimensional image as a map of the metabolic activity of an area of the body. A PET radiotracer is a biological molecule, with a known physiological behavior, whose atom is substituted with its β^+ radioactive isotope without any notable alterations of the chemical and biological behavior of the molecule (George de Hevesy received the Nobel Prize in Chemistry in 1943 for this discovery). Therefore it spreads physiologically within the body after that the radiotracer is intravenously injected into the patient. The decay process of the radionuclide gives rise to the positrons generation. A positron can combine in an annihilation process with an electron of the tissue, emitting two gamma back-to-back photons (511 keV). Thanks to a system of detectors placed around the patient every gamma photon pair is detected causing the input for the image reconstruction. The radioisotope activity distribution is associated with the drug concentration, which in turn provides an insight of the physiology and/or pathology of the patient.

In this chapter the PET technique principles, and those involved in the processes of detection, acquisition, and image reconstruction are explained. On the latter aspect, the problem of spatial resolution and its critical factors is introduced. In the end, the main aspects of Time-of-Flight PET (TOF-PET), a method that assists the image reconstruction, are reported.

2.2 Physical principles of PET operating

2.2.1 Positron emission

As previously reported, PET technique exploits the annihilation of a positron with an electron. This take place after the β^+ -decay of a radioactive nucleus, in which a proton (p) is converted into a neutron (n) by the simultaneous emission of a positron (e^+) and a neutrino (ν_e):

$$p \rightarrow n + e^+ + \nu_e \quad (2.1)$$

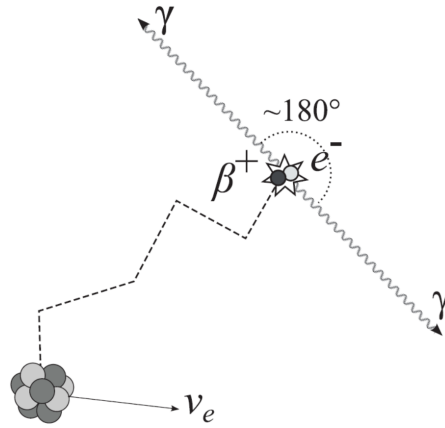


Figure 2.1 Schematic illustration of positron-electron annihilation (taken from [14]).

After the emission from the nucleus, the positrons lose kinetic energy by interactions with the surrounding matter according to the mechanisms of radiation matter interaction. The positron interacts with other nuclei as it is deflected from its original path by one of four types of interaction:

- *Inelastic collisions* with atomic electrons, which is the predominant mechanism of loss of kinetic energy.
- *Elastic scattering* with atomic electrons, where the positron is deflected but the energy and momentum are conserved.
- *Inelastic scattering* with a nucleus, with deflection of the positron and often with the corresponding emission of Bremsstrahlung radiation.
- *Elastic scattering* with a nucleus where the positron is deflected but does not radiate any energy or transfer any energy to the nucleus.

A deflection in the positron path is induced when the positron passes through the matter and loses energy constantly in ionization events with other atoms. If the positron reaches the thermal equilibrium with medium, it combines with an electron of the medium itself, the *positronium*, which is a metastable intermediate species therefore it annihilates emitting two photons of 511 keV photons at 180° to each other in order to conserve momentum, which is close to zero before the annihilation. This mechanism is illustrated in Fig. 2.1.

Two sources of intrinsic uncertainty to this physical phenomenon affect PET analysis, which can not be resolved and which impose a limit on the best achievable spatial resolution:

- The positron range, i.e. the finite distance that positrons travel before annihilating, depending on the atomic number Z , on the density of the medium, and initial energy of the positron. In water, which has a similar composition of human tissues, it is about 1–2 mm.
- The almost collinear emission of the two annihilation photons. The kinetic energy of the positron is determined by the thermal energy which is negligible with respect to the

kinetic energy of the electron since depends on its binding energy. Both positron and electron have not exactly zero momentum during the annihilation. Therefore because of the energy and momentum conservation, many photon pairs are not emitted strictly at 180° . The non-collinear photon fraction has been estimated to be as high as 65% in water [15].

2.2.2 Radiotracer

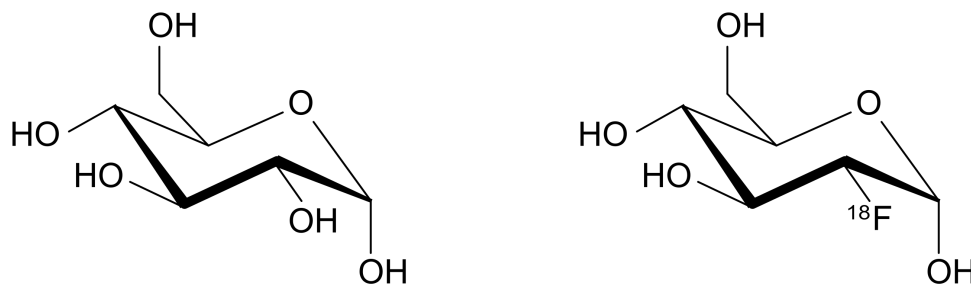


Figure 2.2 Radiotracer molecular structure. The α -D-glucose structure (left) is one on which the Fluorodeoxyglucose (right) is based.

PET is based on several aspects that are strictly related to various Nobel Prize. Especially, the discovery of the positron, by C. D. Anderson: 1936 Nobel Laureate in Physics “for his discovery of the positron”, together with the fundamental theory of the radioactive β decay, forms the theoretical basis of the PET technique. Ernest Orlando Lawrence, moreover, received the Nobel prize in Physics in 1939 “for the invention and development of the cyclotron and for results obtained with it, especially about artificial radioactive elements” and, György Hevesy was awarded the 1943 Nobel prize in Chemistry as he validated the concept that “the changing of an atom in a molecule with its radioisotope will not change its chemical and biological behavior significantly”. These latest discoveries have allowed to have the proper radioisotopes to be used in medical applications, the so-called “physiological radioisotopes” such as ^{11}C , ^{13}N , ^{15}O and ^{18}F , because they are the corresponding stable isotopes of the main constituents of human tissues and indeed are the most used β^+ emitters in PET. Their more relevant physical properties for PET application are listed in Tab. 2.1.

All these isotopes have a short half-life, which has the advantage of delivering a dose into the patient for a short time, the minimum one required for the PET exam. However, there are some disadvantages due to the very short lifetime radioisotopes. For instance, their lifetime might be insufficient with respect to the time necessary for the transport of the radioisotope from the place of production (the cyclotron) to the hospital, since rarely hospitals have cyclotron “on-site”. Where “on-site” means that the delivery time from production to the patient should be in the order of the radioisotope half-life.

The most commonly used radiotracer is the Fluorodeoxyglucose (^{18}F -FDG), its uptake into a living body can be immediately interpreted as the glucose metabolic rate. This because the

Radioisotope	Half-life (min)	Positron average kinetic energy (keV)	Positron average range in water (mm)
^{11}C	20.4	385	1.2
^{13}N	10.0	491	1.6
^{15}O	2.0	735	2.8
^{18}F	109.8	242	0.6

Table 2.1 Physical properties of the most common physiological radioisotopes (adapted from [14]).

positron-emitting fluorine-18 radionuclide is substituted for the normal hydroxyl group (OH^-) at position C-2 in the glucose molecule (see Fig. 2.2).

2.3 Radiation detector for PET

The primary step in PET measurement is to determine the position of annihilation. This can be achieved by measuring, for both γ -rays, the coordinates $P(x, y, z)$ of the first interaction in a detector, which gives the input for the image reconstruction. Then, the ideal PET detector must be able to [6]:

- stop the γ -rays;
- recognizes the position of the first interaction of the photon inside the detector itself;
- evaluate the deposited energy in the interaction (or in the series of interactions);
- record the information about the arrival time, necessary for the coincidence measurement.

During the years different detectors have been developed to provide all these information. However, today, the most reliable solution is the employment of a scintillating material coupled to a photodetector.

2.3.1 Radiation detectors

Scintillating detectors consist of a crystalline material that, interacting with charged particles, produces scintillation light, in the range of vis/UV light. These low-energy photons are then detected by photodetectors and converted into an electrical pulse without losing the original energy information. The ideal scintillation material should possess the following properties:

- high scintillation efficiency to convert the kinetic energy of ionizing radiation into detectable light;
- the light yield should be proportional to deposited energy over as wide a range as possible;
- the medium should be transparent to the emitted wavelength for good light collection;

Material	Density (g/cm ³)	Light yield (ph/keV)	Decay time (ns)	μ_{511keV} (cm ⁻¹)	Photofraction at 511 keV
NaI:Tl	3.67	41	230	0.34	17%
BGO	7.13	8.2	300	0.96	40%
LSO:Ce	7.40	30	40	0.87	32%
LYSO:Ce	7.10	32	40	0.82	30%
GSO:Ce	6.71	8	60	0.70	25%
YAP:Ce	5.37	~21	27	0.46	4.2%
LuAP:Ce	8.3	12	18	0.95	30%
BaF ₂	4.89	1.4 (fast) 9.5 (slow)	0.6 (fast) 630 (slow)	0.43	
LaBr ₃ :Ce	5.08	63	16	0.47	15%

Table 2.2 Properties of scintillating materials used in PET (adapted from [14]).

- its time response should be short so that fast signal pulses can be generated;
- the material should be of good optical quality and subject to manufacture in sizes large enough to be of interest as a practical detector;
- its refractive index should be near that of coupling surface of the light sensor to permit efficient optical coupling with it;
- low cost of production to have a cost-effective scale-up;
- has no background radiation due to internal radioactivity (such as LYSO crystals).

No material simultaneously meets all these criteria, and the choice of a particular scintillator is always a compromise among these and other factors. For what concerns the choice of the most appropriate scintillator for PET, it is crucial measuring the original energy of the incident γ -ray, then all the energy must be released inside the scintillator, preferably in a single photoelectric interaction. To obtain this, the compromise should fulfil high density (and high effective atomic number), linear attenuation coefficient at 511 keV (μ_{511keV}) in the range of 0.3–1 cm⁻¹, high photofraction (i.e. the relative probability between photoelectric and total interaction process) and good light yield. Moreover, as will be explained later in this chapter, short decay times are necessary firstly for correctly identify coincidence events but even more if the timing information is used in the image reconstruction to improve the spatial resolution of PET.

The scintillating materials are classified into inorganic and organic scintillator and as described in paragraph 1.3.2, their scintillation mechanism is different. Until today, solid inorganic scintillators are employed for almost all PET scanners because they meet the aforementioned properties better than organic ones [14]. The most widely used for PET are listed in Tab. 2.2 together with their main relevant properties for PET application.

Since the scintillating features are affected by chemical composition and electronic structure, new materials and new approaches outside the scope of traditional scintillators are emerging.

For instance the metal-organic frameworks (MOFs) nanomaterials scintillators, which could potentially offer the desired level of structural control.

2.3.2 Photodetectors

Photodetectors are sensors that allow converting the light output of a scintillation pulse into an electric signal preserving the original energy and timing information. One of the most commonly used photodetectors is the *PhotoMultiplier Tube (PMT)*, which was also the photodetector chosen for commercial PET scanner up to recent years when silicon-based photomultipliers gained popularity. In its simplest form the PMT is made of a vacuum glass chamber (at least 10 mm in diameter) containing a series of electrodes called dynodes. The inner surface of the glass entrance window is coated with a thin layer of a material, called photocathode, able to absorb light and having a low work function so that electrons can be easily liberated as energy is deposited on it (photoelectric effect). Each photoelectron is accelerated toward the first dynode by a negative potential difference. Therefore the kinetic energy of the electrons increases. In order that for each electron hitting dynode are emitted 3-4 secondary electrons, each dynode is held to a higher potential than the previous one by a voltage divider resistor chain. After 8-12 acceleration steps, depending on the number of dynodes, each photogenerated electron produces around 10^6 secondary electrons that are collected by an anode on the opposite side of the photocathode (typical amplification factor of a PMT) and the amplified signal of the incoming light is obtained. The explained mechanism is schematized in Fig. 2.3. High multiplication factor, low noise, fast response, and low cost are the main factor that made great the PMT. The main disadvantages are the low efficiency of light collection, the sensitivity to the electrical and magnetic field, the high power consumption, and the spread in transit time which degrades the time resolution of the pulse. Indeed, recent advances in the development of semiconductor photodiodes have led to the substitution of PMTs in some applications, including PET. In general, photodiodes have higher quantum efficiency (probability of emitting an electron for each scintillating light photon reaching the photodetector), lower power consumption, are not affected by magnetic fields, and have a more compact size than PMT. The reduced space in which charges move is reflected in a less time spread, making these devices suitable for the characterization timing properties, for instance, the coincidence.

Photodiodes are devices based on p-n junction principles and are made of semiconductor materials such as silicon or gallium arsenide. When light photons hit the semiconductor with an energy comparable to that of the gap between the valence and conduction band, electron-hole pairs are generated and then collected. The conversion is not limited by the need for charge carriers to escape from a surface as in a conventional photocathode, so the maximum quantum efficiency of the process can be several times higher than in a PMT (as 60-80 % instead of ~30 %) besides the fact that spans a much wider wavelength range and, therefore a much higher primary charge is usually created by the light from the scintillator than in a conventional PMT. However, there is no amplification stage in a conventional photodiode, so the electric signal is smaller by orders of magnitude than that of PMTs. This was solved by a multiplication process within the photodiode. Hence, applying a reverse voltage above on the diode, the inner electric field becomes so high that the electrons can gain enough energy to create secondary e-h pairs via impact ionization. Therefore, this effect leads to the formation of a high number of charge

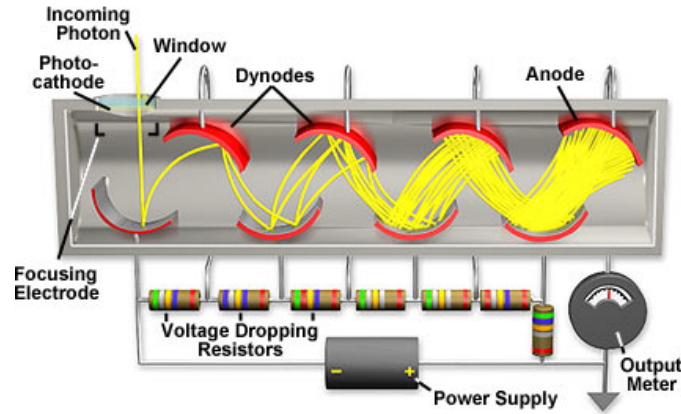


Figure 2.3 Schematic illustration of the working mechanism of photomultiplier tubes (taken from [16]).

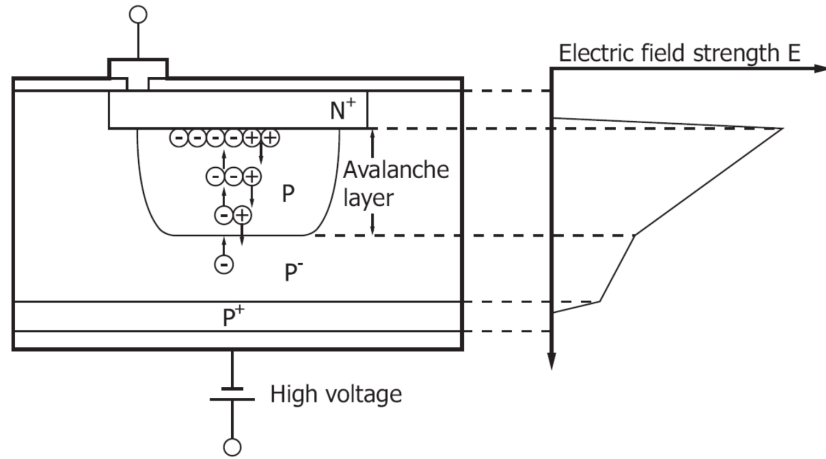


Figure 2.4 Schematic illustration of the working mechanism of avalanche photodiodes (taken from [17]).

carriers in a very short time, in fact, it is called the avalanche effect. Photodiodes based on this mechanism are called *avalanche photodiodes (APD)*. In the APD only the electrons can generate secondary e-h pairs, but not holes because of their higher effective mass. The device shows a measured current proportional to the number of detected photons or generated e-h pairs. Because only electrons have enough kinetic energy to create additional e-h pairs, the avalanche only flows in one direction and is self quenched [19]. The Fig. 2.4 illustrates a schematic of an avalanche mechanism in an APD.

If the applied reverse voltage is increased above the breakdown voltage, holes will gain enough velocity in order to create secondary e-h pairs. This is the *Geiger-mode*, in which a single generated carrier can trigger a self-sustaining avalanche process. In this case, there is a loss of proportionality between the measured current and the number of detected photons.

Avalanche photodiodes allow, compared to the conventional ones, better signal-to-noise ratio

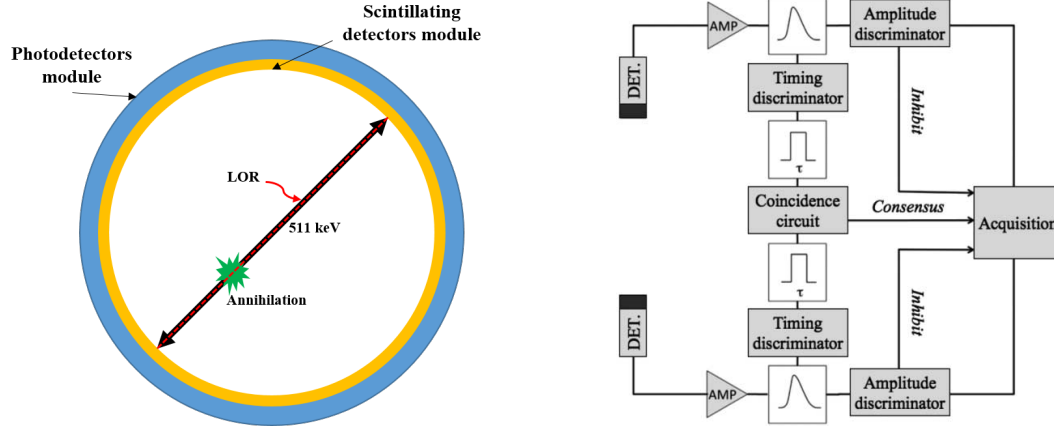


Figure 2.5 Left: section view of a PET system in a schematic representation. Right: Scheme of a simplified data acquisition system for a PET with two detectors only (taken from [14]).

(SNR) and better energy resolution. As demonstrated by B. J. Pichler *et al.* [18], APDs if coupled to fast scintillators (such as LSO), have also good time resolution, about a few nanoseconds (from 1.1 ns to ~ 4 ns).

Further developments have led to exploit arrays of many small avalanche photodiode cells, working in Geiger-mode *silicon photomultiplier (SiPM)*. Since Geiger-mode involves loss of proportionality between the primary and the multiplied charges, SiPMs are used only in counting systems; however, the very small size of the single cells (~ 10 - $100 \mu\text{m}$) allows to preserve the original energy information. Indeed, these cells are small enough so that the probability that a given cell is hit by a scintillation pulse is low, and at most a single photon is incident on a typical cell. Consequently, the number of cells producing an avalanche is proportional to the number of scintillating photons [7, 14]. More details on SiPM performances and applications can be found in [19].

2.4 PET system

2.4.1 PET scanner and acquisition system

Historically, PET systems are generally built as circular “rings”. The earliest tomographs consisted of few detectors (scintillating detectors coupled with photodetectors) that rotating and translating were able to obtain a complete set of projection data, but soon full ring systems were developed. The γ photon pairs generated by the positron-electron annihilation are simultaneously detected by matching in coincidence each detector, constituting the PET system, with its opposite of the ring. This is the so-called *coincidence detection* and thus allow to determine the *Line-of-Response (LOR)* for each event, i.e. the line on which the annihilation is occurred (see Fig. 2.5). If the coincidences among detectors belonging to two different rings are not allowed and only a single ring records the events, a 2 D image will result, otherwise, a 3 D image can be obtained [14].

A typical PET data acquisition system can be described as a two-branch structure. On one side there is the timing circuitry and on the other side the one providing position and energy signals. In particular, for each pulse coming from a photodetector its amplitude (which is directly proportional to the corresponding charge generated by the photon within the photodetector [7]) is analyzed. If the amplitude is consistent with a signal from a 511 keV γ -ray, the arrival at a certain time (within the coincidence window) of the second signal with the same amplitude can be analyzed and the event is acquired. Otherwise, if this succession does not occur the event is discarded. A simplified scheme of PET data acquisition system with only two detectors is illustrated in Fig. 2.5. This concept can be extended to a multiple detector system implementing a more complex coincidence circuit.

2.4.2 Parameters of PET scanner

The performances of a PET scanner are defined by four main parameters: spatial, energy and time resolution, and sensitivity.

Spatial resolution

The spatial resolution of PET, as discussed in paragraph 2.2.1, is limited by the intrinsic uncertainties in the physics of β^+ -decay which is a factor that can not be improved. Among the other factors that degrade it the main are: the finite size of the detectors and multiple crystal interactions or coding errors. The first leads to the LOR to be not a line but an interval inside which the annihilation has a non-zero probability to occur, and to the occurrence of a parallax error if no information about the Depth-of-Interaction (DOI). The seconds give rise to the incorrect identification of the detector where the annihilation occurred. Moreover, the spatial resolution of a PET system is not constant along the whole *Field-of-View (FOV)*, which is the region of space that is sufficiently sampled to provide a full set of LORs for the tomographic reconstruction. The spatial resolution can be therefore summarized, in terms of Full-Width at Half-Maximum (FWHM), with the following formula [14, 20]:

$$FWHM = 1.25 \sqrt{(d/2)^2 + s^2 + (0.0044R)^2 + b^2 + \alpha^2} \quad (2.2)$$

where d is the size of the detector, s is the positron range, $0.0044R$ is the blurring related to the positron range, b is the crystal decoding error factor, R the detector system ring radius and α is a factor that takes into account the depth of interaction (DOI), the radial variability of FWHM and depends on the detector material. For standard clinical PET scanners, the spatial resolution is 1–4 mm [14].

Energy resolution

The energy resolution (R) is another figure of merit of a PET detector and is defined as how is reported in the scintillator section (see paragraph 1.4.4). In PET applications a good energy resolution is essential to discriminate the 511 keV photons from the background but also for discarding the γ -rays scattered inelastically that degrade the determination of the exact positron-electron annihilation position.

Time resolution

The stochastic process of light emission of a scintillator is defined by its decay time and light yield. They are the two main elements limiting the time resolution (τ) of PET scanners. Their influence on the time resolution can be described as:

$$\tau \propto \frac{(\tau_d)^\alpha}{\sqrt{N_{ph}}} \quad (2.3)$$

where τ_d is the decay time, N_{ph} the number of light photons detected and α is a constant in the $0 < \alpha < 1$ range, whose value is commonly assumed to be $\alpha = 1/2$.

Other components affecting the time resolution are the rise time of the scintillation pulse, the light transport properties of the scintillating materials and the time spread added by the photodetectors.

A pair of detected γ -rays to be identified as coincidence events and to avoid the loss of their detection, their *time window*, i.e. their maximum difference in time, should be at least two times the time resolution. For standard clinical PET scanners, the time resolution is of the order of few nanoseconds [14].

Detection efficiency

Detection efficiency refers to the efficiency with which a radiation measuring instrument converts emissions from the radiation source into useful signals from the detector. Maximum detection efficiency is desirable to have the best signal-to-noise ratio with a minimum amount of radiotracer injected into the body.

The detection efficiency D of a radiation counting system can be defined as:

$$D = \frac{K}{A} \quad (2.4)$$

where K is the counting rate and A is the source activity. The detection efficiency is affected by several factors and can be written as [14, 21]:

$$D = \eta_{geom} \times \varepsilon \times f \times F \quad (2.5)$$

where η_{geom} is the geometrical efficiency, ε is the intrinsic detection efficiency (i.e. the product of the intrinsic efficiencies for 511 keV γ -rays of the two detectors involved in the coincidence), f the electronic recording efficiency and F a factor which account for the absorption and scattering in the object. Some factors of the detection efficiency affects the spatial resolution indirectly. Their improvement for D can be detrimental to the spatial distribution. Especially, the geometrical efficiency η_{geom} , which is related to the solid angle coverage of the PET ring, can be increased by reducing the diameter or increasing the axial extension of the PET scanner. However, the parallax effect worsens as the scanner radius is reduced. In turn, the axial extension can lead to an increase in the scattered events. The intrinsic detection efficiency can be improved by increasing the thickness of the crystal, but, once again, spatial resolution would be degraded by the increased parallax effect [14].

2.5 Image reconstruction

2.5.1 Standard PET scanner

The aim of a PET scan is the measurement of activity distribution $\rho(x, y, z)$ of the radiotracer injected into the body patient. Thanks to the nearly-collinear generation of the γ -ray pair from the positron-electron annihilation it is possible to define a line L along which the annihilation occurred, the Line-of-Flight. Measuring the number of projection N along the LOR connecting a detector i to a detector j can be obtained the activity distribution since this and projections are linked by the line integral operator. Since the detectors have a finite size there is no unique Line-of-Response (LOR) that connects a couple of detectors. Thus all the possible LORs connecting two crystals define a fraction of the Field-of-View seen by two coupled detectors, i.e. the *Volume-of-Response* (VOR). Therefore the value of the activity distribution in every single VOR (λ_j) is defined by

$$\lambda_j = k \int_{VOR_j} \rho(x, y, z) dV \quad (2.6)$$

Various techniques and algorithms are used to reconstruct the images of activity distribution from the complete set of projections measured at different angular views around the object. Among the most common techniques there are the *filtered Back-Projection* (FBP) and the *maximum likelihood expectation maximization* (ML-EM). The first is used in 2 D PET and the second for 3 D one. Details about algorithms used in reconstruction process are in [14, 2].

2.5.2 Time-of-Flight PET (TOF-PET)

As seen, the algorithm so far mentioned are not the best resource to have an image of quality. A large number of clinical studies have unequivocally demonstrated that a significant improvement concerning image quality and better signal-to-noise ratio (SNR) can be achieved by the use of the difference of the arrival times of the two annihilation photons, i.e. the time-of-flight (TOF). Ideally, the exact position of the annihilation might be determined from the difference of arrival time of two γ photons onto opposing detectors placed at a distance D (see Fig. 2.6).

D is the distance between the two opposing detectors that reveal the γ -ray pair.

If the time of arrival of the two photons emitted from point C to detector A and B can be written as $T_A = dA/c$ and $T_B = dB/c$, the difference in arrival time is then given by:

$$\Delta T = T_A - T_B = \frac{dA - dB}{c} = \frac{2\Delta S}{c} \quad (2.7)$$

where dA and dB are the distance from the annihilation point to the corresponding detector, ΔS the displacement of the annihilation point from the center and c is the speed of light.

Then, inverting Eq. 2.7 and measuring the time difference ΔT the ΔS with their respective tolerance can be get:

$$\Delta S = \frac{c\Delta T}{2}; \quad \sigma_S = \frac{c}{2} \sigma_T \quad (2.8)$$

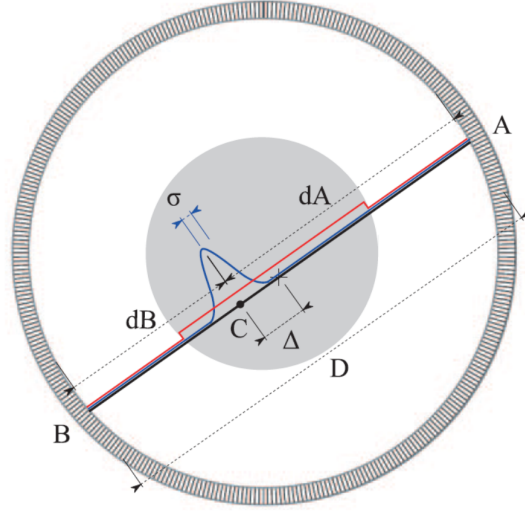


Figure 2.6 The Time-of-Flight PET concept. Non-TOF data (red) are evenly distributed along the LOR while TOF-data are distributed around the annihilation point. Thus the SNR in the reconstructed image increases (taken from [14]).

where σ_s and σ_T are respectively the spatial and time uncertainty. Therefore, an high precision in determining the difference of the arrival time is reflected on a better spatial resolution.

This technique is called *Time of Flight PET (TOF-PET)* because it makes use of the difference in the time of arrivals of the photons onto the opposing detectors. In TOF-PET scanners that have a time resolution of about 500 ps (FWHM), it would be possible to measure the position of the annihilation point with a precision of ~ 7.5 cm (FWHM). More recent developments in fast detectors lead to a time resolution or coincidence time resolution (CTR) in clinical whole-body TOF-PET scanner to be about ~ 215 ps FWHM (Siemens Biograph Vision PET/CT [3]), which means a spatial uncertainty along the line-of-response of ~ 3 cm. Note that the current time resolution values of commercial PET scanners do not allow a sufficient spatial resolution along the LOR to avoid an algorithm for reconstruction-less PET imaging. However, the studies have been proved [22] that TOF reconstruction converges more quickly and difference of the arrival time information improves the signal-to-noise ratio as:

$$SNR_{TOF} = \sqrt{\frac{d}{c\Delta T}} SNR_{no-TOF} \quad (2.9)$$

where d is the effective patient diameter.

Finally, considering the physics of β^+ emission and the positron range in human tissues (1-2 mm) the best achievable spatial resolution along the LOR is about 1.5 mm which limits the CTR to be about 10 ps.

2.6 Improving Time-of-Flight PET (TOF-PET)

2.6.1 Introduction

Time-of-flight (TOF) measurement was suggested as early as 1969 by Brownell *et al.* [23]. The first practical scanners using this technology were built in the early 80s where CsF and BaF₂ have been employed as scintillators. At the system level, the measurements between 470 and 750 ps were reached. However, while the light scintillation properties of CsF or BaF₂ were favorable for TOF performance, both the scintillators had a low density that prevented the possibility of high spatial resolution and sampling.

The need for high spatial resolution led to the parallel development of non-TOF PET during the late 70s and early 80s and making the bismuth germanate scintillator (Bi₄Ge₃O₁₂ or BGO) as standard in positron emission tomography (PET), thanks to its high detection efficiency and acceptable light output. However, its long decay time (300 ns) and low light output (~ 8 ph/keV) made it unsuitable in TOF-PET. Therefore, with the success of BGO-based PET systems, which enabled higher spatial resolution and sensitivity (although lower count rate than CsF or BaF₂), TOF-PET development came to a halt.

In the 90s, the study of new scintillators led to light the properties of the Cerium-doped lutetium oxyorthosilicate or LSO (Lu₂SiO₅:Ce). These have allowed the birth of a new phase of TOF-PET research and development [24]. Nowadays, time resolution in clinical TOF-PET scanner has come to be about 210 ps allowing a great improvement of the reduction of noise and to the spatial resolution [3]. The 10 ps limit, which allows a reconstruction-less PET imaging is still far but great efforts are being made to reach it.

2.6.2 Advantages of improved time resolution

As is mentioned the TOF-PET technique exploits the time information to assist the reconstruction process. In the paragraph 2.5.2 the improvement in the SNR (see Eq. 2.9) has been highlighted and in the following it possible to appreciate a brief look about the resulting advantages, inspired to Conti *et al.* [22].

Reduction of examination time and dose

The noise equivalent count (NEC), which is a common image quality index in PET is resulted to be proportional to the square of the SNR as is reported by S. Strother *et al.* [25]:

$$NEC \propto SNR^2 \quad (2.10)$$

Considering the study of Conti *et al.* [22], the Eq. 2.10 and 2.9, it notes that there is an improvement in terms of noise and contrast with the same counts from the non-TOF image to the TOF one. This can be view related to the reduction of PET examination time and the dose injected. In particular, reducing the dose of a PET examination will reduce the cancer risk both by radiation exposure for the patients and occupational radiation exposure of professionals in the clinical environment.

Improvement of spatial resolution

Typically whole-body oncology scan is only 1–3 min per bed position to keep comfort and patient workflow, resulting in low sampling. In order to partially compensate a low statistics, in standard PET scanners, an image pixel size larger than its limit is preferred to have more counts per pixel and obtain a lower noise image. Thanks to the gain in SNC with TOF (from Eq. 2.9) it can take advantage of pixel size reduction without sacrificing comfort, workflow, or stats, but rather lead to an improvement in spatial resolution.

Patient size equalizer

In oncology practice, typically a longer acquisition time is needed for a larger patient which is characterized by higher attenuation and hence by more noise. Often the longer acquisition time does not compensate for the poor quality of the data. However, as a direct consequence of the Eq. 2.9 the SNR for TOF examination is greater for larger patients. Therefore TOF acts as an equalizer, allowing to reach an image quality in larger patients close to those of average size.

2.6.3 Coincidence time resolution (CTR)

The key parameter that defines the performance of a TOF scanner is the *coincidence time resolution* (CTR). To delineate this figure, a system as reported in Fig. 2.7 can be considered: two independent detectors are irradiated by a common radioisotope source that is assumed to emit at least two detectable quanta in *true coincidence*; that is, both radiations arise from the same nuclear event within the source. Furthermore, if there is no appreciable time delay between their emission then the resulting spectrum from this measurement will be similar to that in Fig. 2.7. A fraction of all the true coincidence events emitted by the source are detected simultaneously by both detectors and they will appear in the same region of the time spectrum, giving origin a *prompt coincidence* peak. The area under this peak gives the total number of detected coincidences instead, its full-width-at-half-maximum (FWHM) has the contribution of the CTR of the two detectors considered. As resolution is greater than that of the single detectors. Amplitude walk and time jitter, for example, are not identical in both branches and therefore contribute to broad the distribution.

If detectors, triggering conditions, and timing electronics are nearly equal in both branches, then the prompt coincidence peak should be symmetric. While, if one branch differs substantially from the other, then asymmetric prompt coincidence peaks often result [7].

2.6.4 CTR contributing factors

Many factors affect the CTR. To improve the TOF-PET and exploit its benefits it needs to understand the full detection chain (see Fig. 2.8). In the following paragraphs, a brief overview of these contributions is reported.

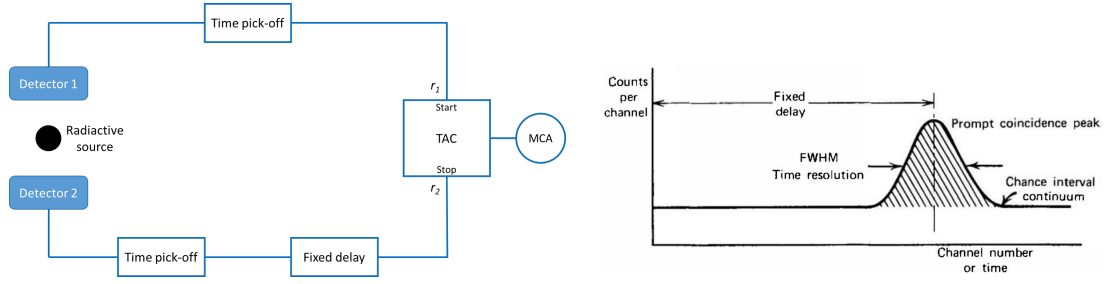


Figure 2.7 Definition of the coincidence time resolution (CTR). Left: a simplified system to record time spectra from a radioisotope source emitting coincident radiation. Right: simplified spectrum for a radioisotope source emitting some radiation in prompt coincidence (adapted from [7]).

Depth of interaction

The *depth of interaction (DOI)* corresponds to the distance that is interposed between the point in which a photon hits the detector and that in which it interacts with the medium. Since it can assume different trajectories in the medium before interacting with it, the DOI is not a constant and predictable value. This uncertainty leads having different possible interaction times.

Scintillation process

The time resolution depends on the rate of photoelectrons above the detection threshold, which in turn depends on the time distribution of photons being converted in the photodetector.

The main parameters influencing the time resolution of a scintillator detector are the light yield LY_{out} , the rise and decay time of the scintillation process (τ_r and τ_d respectively) as illustrated by the following formula, derived by the Hyman theory:

$$CTR \propto \sqrt{\frac{\tau_r \tau_d}{LY_{out}}} \quad (2.11)$$

As it was explained in paragraphs 1.4.1 and 1.4.3, the light yield depends on the scintillator material and the rise and decay time depend on how fast their states may be populated and return to the equilibrium conditions. Thus, in order to enhance the CTR, scintillators with high light yield and a fast scintillation process should be exploited.

Light transport and collection

Since the photons are emitted isotropically there are large variations between the different optical path lengths for their different trajectories, as illustrated in Fig. 2.8. This results in a *photon transit time spread (PTS)*, which degrades the timing resolution. Moreover, the refractive index mismatch between the scintillation material and the coupling medium to the photodetector (typically close to 1.5) leads to a high probability for about 2/3 of the photons to bounce in the scintillator up to several times before being extracted. Indeed, to decrease the difference in

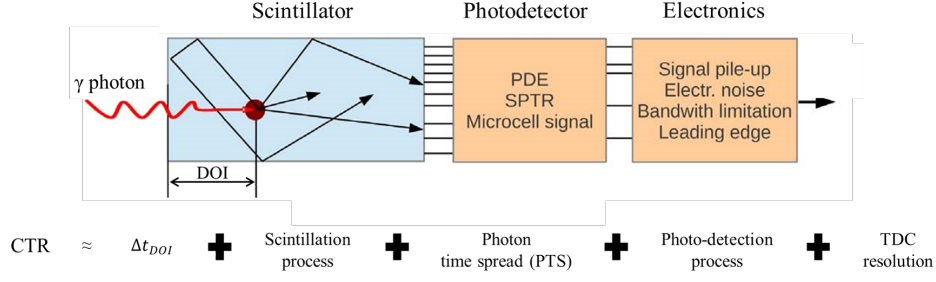


Figure 2.8 Process involved in the detection of γ photons showing the different contributions to the time resolution in terms of radiation matter interaction, scintillation mechanism, light transport in the medium, photo-detection process, and readout electronics (adapted from [27]).

refractive index between the two coupling mediums, and enhance the light collection, the scintillators are often wrapped in a reflector and coupled with the photodetector window through an optical grease or a glue.

Concerning the increase in PTS, a longer path length increases the probability for the photons to be absorbed, affecting, therefore, the *light transfer efficiency (LTE)* to the photodetector, and hence leading to a less number of photon extracted and consequently to a worse CTR [26].

Photo-detection process

The *photo-detection efficiency (PDE)* determines the number of photons coming from the scintillator and converted in photoelectrons thanks to the photodetector. Presently many SiPM producers reached very high and comparable PDE values up to 60% [19], however, a fraction of photons are lost in the conversion process and do not produce any photoelectron signal, which is the actual carrier of timing information. Then the PDE affects the statistic of the final signal and its time resolution.

The *single photon time resolution (SPTR)* is another important parameter that is involved in the signal goodness in the case if a SiPM is used as a photodetector. This is influenced by the fluctuations between different avalanches generated in the same conditions due to the dark count rate, crosstalk, and after pulses. The latter two are generated by the avalanches which originate optical photons due to intraband luminescence. Then they can trigger secondary avalanches [26, 19].

Electronic readout

Finally, in order to digitize the electronic signal and determine the arrival time of each photon a time-digital-converters (TDC) is connected to the SiPM. Therefore the intrinsic time resolution and noise of the TDC are other factors playing a role in the overall time resolution.

Chapter 3

Metal-organic frameworks

3.1 Introduction

Metal-organic frameworks (MOFs) are hybrid porous materials that consist of a regular array of positively charged metal ions or clusters that are coordinated by organic molecules, called ligands. The overall array is, therefore, a repetition of building blocks in cage-like structure and spans in one, two, or three dimensions [28]. The hollow structure allows them to have an extraordinary large internal surface area, typically ranging from 1000 to 10000 m²/g, thus exceeding those of traditional porous materials such as zeolites and carbons [29]. Thanks to the remarkable self-assembly properties of MOFs it is possible to control the growth of crystalline frameworks and also their porosity. Furthermore, a variation of the organic component of MOFs allows additional structural modifications, as well as electronic, optical, and chemical properties. These aspects have made MOFs ideal candidates for the storage of fuels (hydrogen and methane), the capture of carbon dioxide, and catalysis applications, to mention a few. Therefore, the ultimate flexibility with which the metal units and organic linkers can be varied has led the MOFs to be suitable for a wide range of potential uses. Indeed, thousands of structures are being prepared and studied each year (Fig. 3.1). Especially exploiting the fluorescence and the scintillation of several conjugated organic molecules, a particular interest for MOF nanocrystals based on fluorescent ligands (nano-MOFs) is born in the last years in order to apply them in the field of photonic, optoelectronic, and biomedicine but also in detectors [4].

In this work, nanocomposite scintillators based on MOF nanocrystals have been investigated. The synthesis and the optical characterizations have been performed at the Materials Science Department (UNIMIB). The accurate investigation on their scintillation properties related to the TOF-PET imaging has been carried out in the CERN Crystal Clear laboratory in Geneva, Switzerland.

In the following paragraphs, an overview of the composition, geometries, and synthesis of the studied nanocomposites is presented. Additionally, the physical aspects of the scintillation process on which they are based are treated.

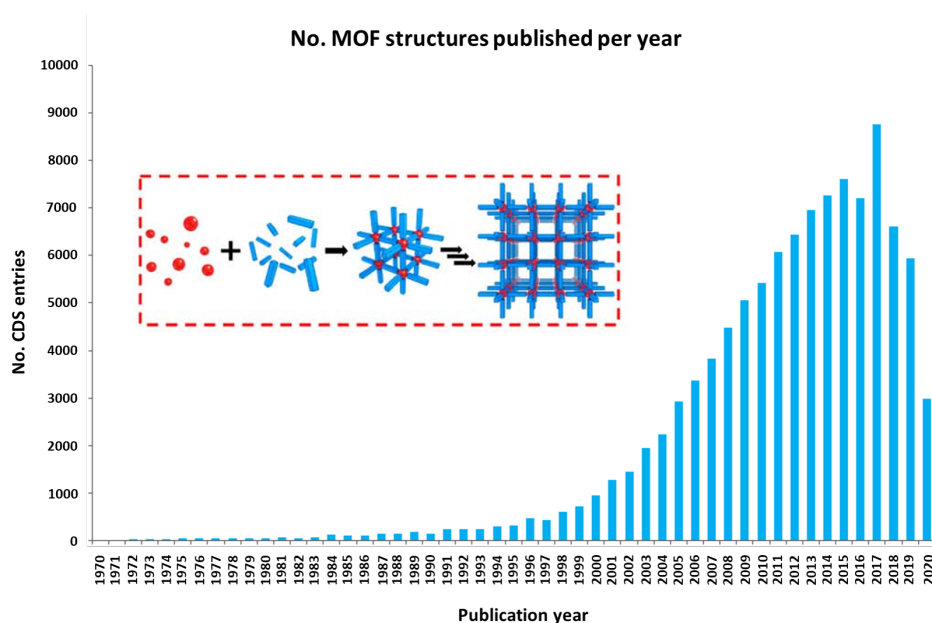


Figure 3.1 Metal-organic framework structures reported in the Cambridge Structural Database (CSD) from 1970 to 2020. The inset shows the MOF self-assembly process from building blocks: metals (red spheres) and organic ligands (blue struts). Adapted from [30].

3.2 Metal-organic frameworks-based composite in the case study

3.2.1 Composition

The Zr-oxo-hydroxy has been used as a metal cluster node since it presents excellent thermal and chemical stability, which are crucial properties for the devices. Its effective atomic number of $Z_{eff} \simeq 40$ is high enough to have a good interaction with the ionizing radiation. Then, the fluorophore dicarboxy-9,10-diphenylanthracene (DPA) has been utilised as emitting ligand to exploit its high fluorescence quantum yield (0.96) and sharp absorption and emission spectra thereby mitigating emission reabsorption [31]. Its absorption spectrum is in the near-UV interval, which is a typical emission range of wide-gap metal oxide. Thus Zr-based cluster may sensitize the ligand luminescence by energy transfer as it is reported in the case study of A. Monguzzi *et al.* [5] related to (anthracene-9,10-diyl)dibenzoate (ADB)-based MOFs, where the ADB molecule is a derivative of the DPA.

The nanocomposites have been embedded in a polymer matrices: poly(methyl methacrylate) (PMMA) and poly(dimethylsiloxane) (PDMS). They are both inert to the processes involved in the scintillation and are transparent in the near UV–vis spectral range. Their density is similar but mechanical and structural properties are distinct. The first is a rigid, amorphous glassy polymer ($T_g > 100^\circ\text{C}$, $n = 1.50$ at 450 nm), while the second has an elastomeric nature ($T_g < -100^\circ\text{C}$, $n = 1.44$ at 450 nm) [32].

The flexibility with which the two polymers can be handled offers suitable shape and quality of scintillators. This is a big advantage compared to inorganic crystals which need to be cut and



Figure 3.2 First pixel of PMMA matrix with different concentrations of MOF: 0.05 %_w (left) and 0.5 %_w (right).

polished to reach the same final structure. It means a decrease in costs and time in processability.

Furthermore, A. Monguzzi *et al.* [5] speculated that the polymers can shell the nanocrystals by saturating the dangling bonds due to under-coordinated ligands or metal ions on the crystal surfaces. They noticed an increase in the quantum yield after embedding the MOFs in the polymer.

3.2.2 Geometries employed

To study the scintillation response of the nanocomposites, samples with different amounts of MOF in weight have been investigated. In first, pad samples, both those based on PMMA and PDMS ones, have been realized with 10 mm in diameter and 5 mm in height. Since certain setups the samples have to be coupled with a SiPM (photodetector) of $3 \times 3 \text{ mm}^2$ and to be placed close to the radioactive source, then the ideal was to have pixels of about $2 \times 2 \times 3 \text{ mm}^3$. Therefore, the pads have been cut to reach the desired shape, at CERN laboratories (Fig. 3.2).

Whereas, at a later time, the cylindrical pillars have been realised directly of 3 mm in diameters. Cutting them, rods of $\sim 15 \text{ mm}$ of length and pixels of $\sim 3 \text{ mm}$ of length have been obtained (see Fig. 3.3). This permitted to reduce the cutting time and increase the ease of the process. In this case, the elongated geometry did not allow working with the PDMS matrix due to its elastomeric nature.

3.2.3 Synthesis

MOF synthesis

Zirconium-based metal-organic frameworks were synthesized exploiting a modulated approach to control the nucleation and growth of nanocrystalline MOFs. Briefly, the linker 9,10-bis(4-carboxyphenyl)anthracene ($\text{DPA}(\text{COOH})_2$), the zirconium source ZrCl_4 and acetic acid were dispersed in dry dimethyl formamide (DMF). The mixture was heated at 120°C for 22 hours and then cooled down to room temperature. The whitish powder was filtered and washed with fresh solvents and then activated under high vacuum to obtain highly porous crystalline materials. The

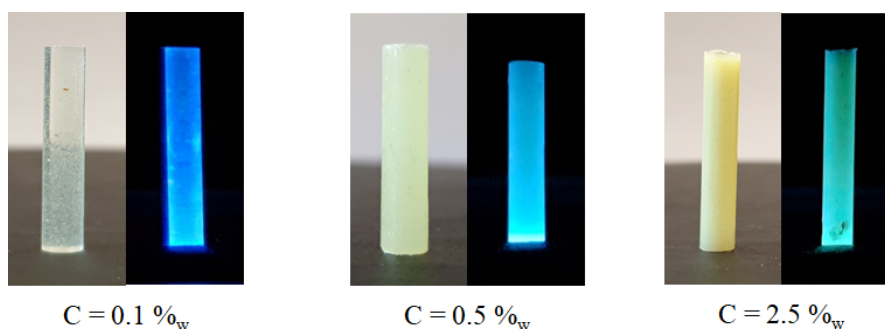


Figure 3.3 Rod-like MOF-based composites with different concentrations: 0.1 %_w (left); 0.5 %_w (center) and 2.5 %_w (right). The left pictures were taken in ambient light conditions, while the right pictures exposing the samples at UV light.

synthesis procedure is schematized in Fig. 3.4b. The reagents and solvents employed in MOF synthesis are reported in Tab. 3.1. In Fig. 3.4a a digital picture of Zr-DPA after the synthesis can be found.

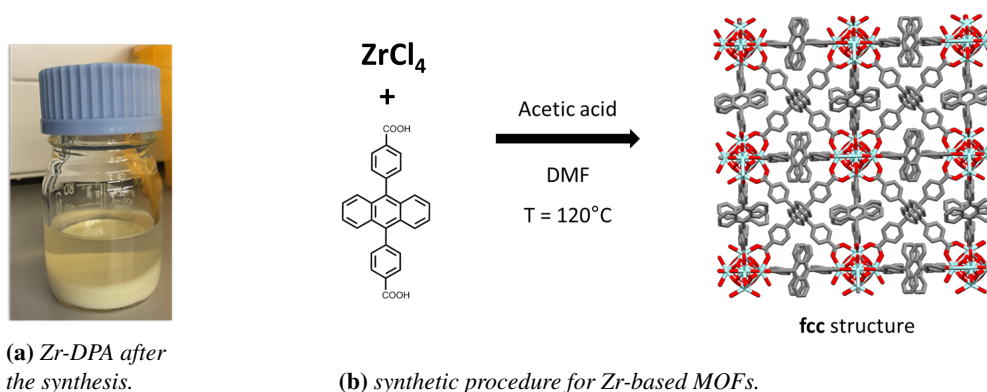


Figure 3.4 Digital picture of sample Zr-DPA after the synthesis (taken from [32]), and synthetic procedure for Zr-based MOFs.

The building blocks from which the MOF structure is composed are high-Z metal-oxo clusters of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{COO}^-)_6$ and emitter ligands based on diphenylanthracene ($\text{DPA}(\text{COOH})_2$). The structure of these building blocks is illustrated in Fig. 3.5a, while that of the overall Zr-DPA MOF is in Fig. 3.5b.

Synthesis of MOF composites based on PMMA and PDMS

Poly(methyl methacrylate) (PMMA) ($T_g = 120^\circ\text{C}$) was dissolved in dichloromethane (40 mL). A proper amount of MOF powder was dispersed in the polymeric solution under vigorous stirring. The solvent was removed under a stream of nitrogen and the polymeric composite was further dried under high vacuum at 80°C . Once dried, the composite was grounded with mortar and pestle, then was charged in a proper glass mold. The mold was heated at 230°C for 30 minutes in

Sample	ZrCl ₄ (mg)	DPA(COOH) ₂ (mg)	Acetic acid (mL)	DMF + H ₂ O
Zr-DPA	116.5	209.0	1.43	50 mL + 50 μ L

Table 3.1 Reagents and solvents employed in MOF synthesis. Right: digital picture of sample Zr-DPA after the synthesis.

a glass oven under vacuum, removed from the oven, and pressed with a custom-made apparatus (see Fig. 3.6). Once cooled at room temperature the sample was removed from the mold.

To obtain self-standing PDMS nanocomposites, the dispersion of MOF nanocrystals has been poured in a specific mold where it has been cured at 60°C. The nanocomposites were obtained by the reaction of vinyl-terminated polydimethylsiloxane with polydimethylsiloxane-co-methylhydrosiloxane by curing at 60°C.

PDMS prepolymer RTV 615 base was poured to a polypropylene tube and a 0.2 mL of a proper amount of the dispersion of Zr-DPA in tetrahydrofuran was added in order to have two samples with two different concentration (0.05% and 0.5% in weight). The mixture was homogenized under stirring and successively RTV 615 curing agent was added. After careful mixing, the homogenous mixture was degassed under vacuum for 2 hours and poured onto a proper polypropylene mold. A second degassing procedure was performed, and the sample was heated under a vacuum oven at 60°C for 16 hours. The specimens were slowly cooled to room temperature and removed from the mold.

The pad-like samples have been realised through a cavity of an encapsulator having 5 mm deep and 10 mm high. Instead, for the rod-like ones has been used a glass cylinder as a mold with an inner diameter of 3 mm.

For further details about synthesis and structure of MOF-based composites see Supplementary Material of [32].

3.2.4 Photophysics of nanocomposite scintillators

In the case of MOFs, where a metal cluster sensitizer interacts with the ionizing radiation and sensitizes the ligand luminescence, a hybrid scintillation mechanism between that of inorganic materials and organic ones takes place (see section 1.3.2).

Free charges are generated by the interaction of the ionizing radiation with the polymer matrix and with MOF nanocrystals, in this case especially with the high-Z ions of the zirconium oxo-hydroxy clusters. They recombine generating radiative singlet states on the organic ligands DPA from which efficient fluorescence is produced and that can be detected by a photon detector. On the other hand, there is also the metal cluster contribution. Further carriers (electron-hole pairs) are generated with the interaction of ionizing radiation and the cluster. Therefore, given the resonance between the ionizing radiation-activated luminescence of Zr-based clusters and the DPA absorption, the formation of fluorescent singlets can be sensitized by energy transfer from excited clusters [5]. The explained mechanism is sketched in Fig. 3.7.

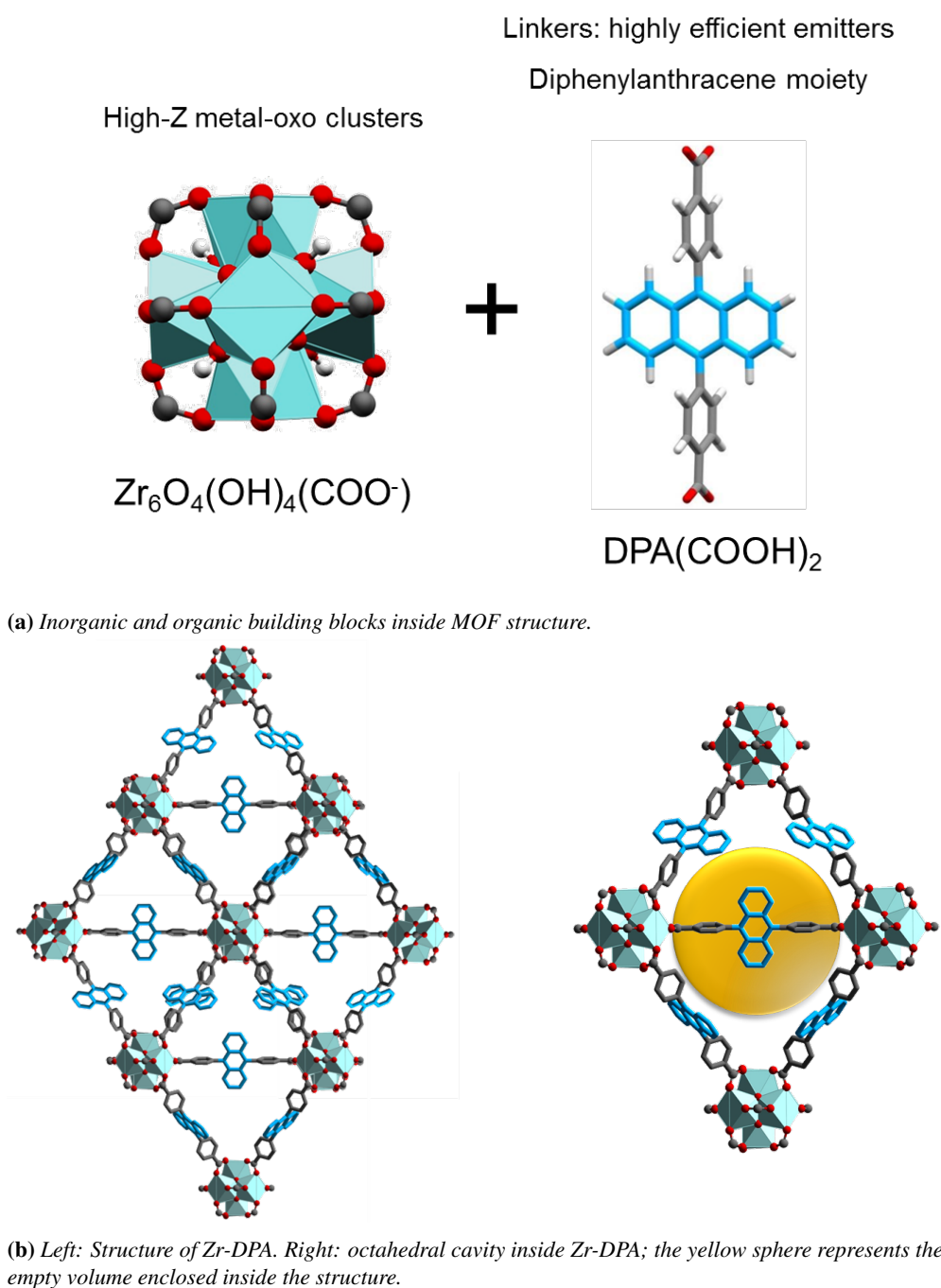


Figure 3.5 MOF structure with its inorganic and organic building blocks inside.

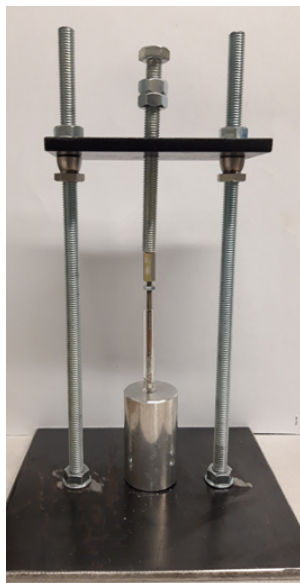


Figure 3.6 Custom-made press for hot pressing MOF:polymer composite cylinders.

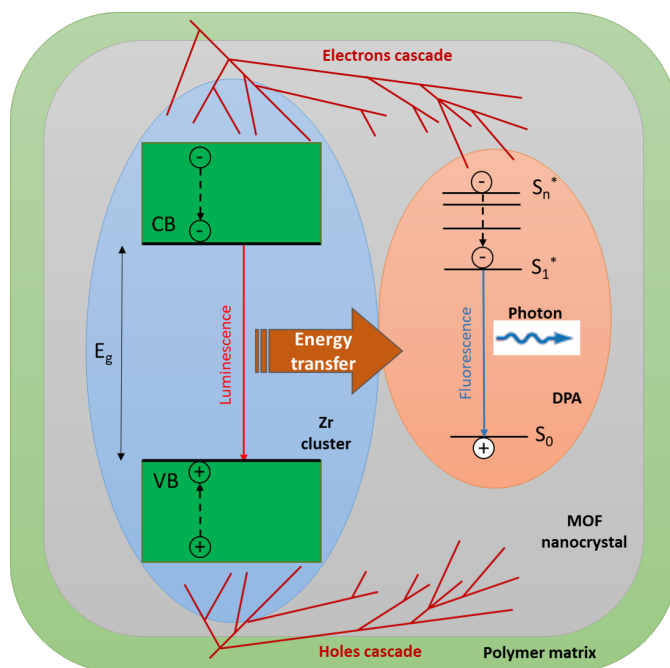


Figure 3.7 Photophysical processes involved in the scintillation emission of the nanocomposite

Chapter 4

Optical and scintillation properties characterization of MOFs-based composites

4.1 Steady state and time resolved photoluminescence

4.1.1 Materials and methods

Steady state PL

Steady state photoluminescence (PL) measurements were performed to study the emission spectra following a fixed wavelength excitation. For such measurements, a Varian Cary Eclipse fluorescence spectrophotometer (Fig. 4.1) was used. It has a Xenon lamp as a source of excitation light. The excitation wavelengths and the ones which were detected are both in the range of 200-900 nm.

Furthermore, with the same setup, photoluminescence excitation (PLE) measurements can be taken setting an emission wavelength and performing a scan of the excitation wavelengths.

PL and PLE measurements were performed on a solution of diphenylanthracene dispersed in tetrahydrofuran (THF). The solution has been placed in a quartz vial with a thickness of 1 mm. The excitation wavelength to study the PL spectrum of the DPA:THF solution has been fixed at 370 nm, while to study the PLE, the emission wavelength has been set at 450 nm.

The same excitation wavelength has been used to study the PL spectra of the pad-like nanocomposites with the PDMS matrix.

Time resolved PL

Time-resolved photoluminescence (TR-PL) measurements were performed in order to investigate the lifetime of the nanocomposites.

These measurements were made using an Edinburgh Instruments FLS980 spectrometer. A pulsed laser was used as excitation source, in particular an EPLED405 diode laser that emits light pulses at 405 nm. The laser repetition rate can be changed since the time between the

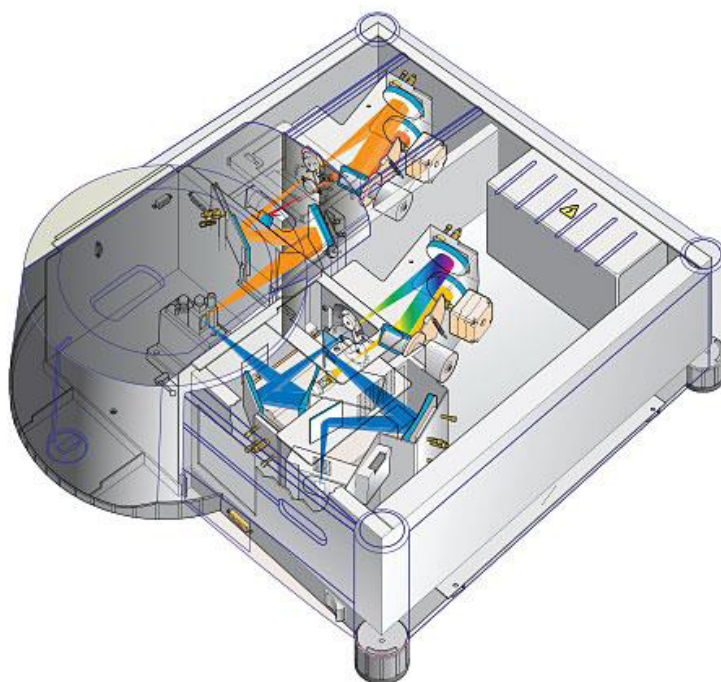


Figure 4.1 Varian Cary Eclipse fluorescence spectrophotometer (adapted from [33]).



Figure 4.2 Image of Edinburgh Instruments FLS980 spectrometer (taken from [34]).

emission of two consecutive pulses must be greater than the time in which the physical process dynamic of the materials takes place.

Experimentally, the lifetime of pad-like nanocomposites with the PDMS matrix has been investigated with this technique. A laser repetition rate of 10 MHz has been chosen.

The study of the rod-like nanocomposite has been performed with a second technique, which offers the possibility to reproduce 3 D contour spectra composed by the emission spectra at

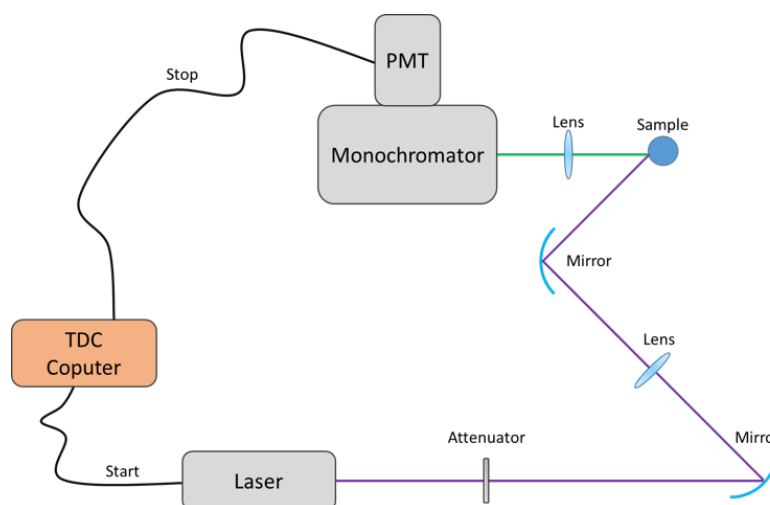


Figure 4.3 Scheme of the experimental setup used to study emission spectra at several decay times

several decay times. Therefore, from this, it is possible to extract information about emission spectra and lifetimes.

Also in this case an EPLED405 diode laser has been used. Its light beam has been modulated through an attenuator. The beam was directed to the sample with a series of mirrors and lenses. The emitted light by the sample was focused with a lens in an Oriel Instruments Cornerstone 260 1/4m monochromator. Its wavelength range is from 180 nm to 24 μm with an accuracy of 0.35 nm and a precision of 0.08 nm. The large wavelength range is obtained with three different gratings mounted into the monochromator. They are individually replaceable through remote control.

The components of light emitted were detected with an Hamamatsu R943-02 PMT having 10×10 mm GaAs:Cs photocathode and synthetic silica window. Thanks to this combination a high sensitivity over the range 300-800 nm was guaranteed with a maximum temporal resolution of 100 ps. The PMT signal was amplified with a Hamamatsu C5594 high-speed amplifier, which has a very high gain of 36 dB and an intrinsic noise of 5 dB only.

4.1.2 Results

In Fig. 4.4 PL and PLE spectra are shown. The different peaks in the PLE spectra are associated with the vibronic structure of the DPA molecules. The PLE maximum is at 370 nm, while the PL maximums are at ~ 405 nm and ~ 430 nm.

The PL spectra of pad-like PDMS nanocomposite are illustrated in Fig. 4.5. The two sides of the PDMS:0.5% MOF pad were not homogeneous. Therefore the PL spectra of the two faces are reported and no significant difference appeared. The maximum of the emission peak is at ~ 445 nm for the PDMS:0.05% MOF and at ~ 460 nm for PDMS:0.5% MOF.

The TR-PL offline data analysis was done by SigmaPlot and ROOT. The PL dynamics of the nanocomposites have resulted in agreement with a fit function having two exponential decay components (Eq. 4.1). To perform the fit just the portion of the decay curves beyond the intensity

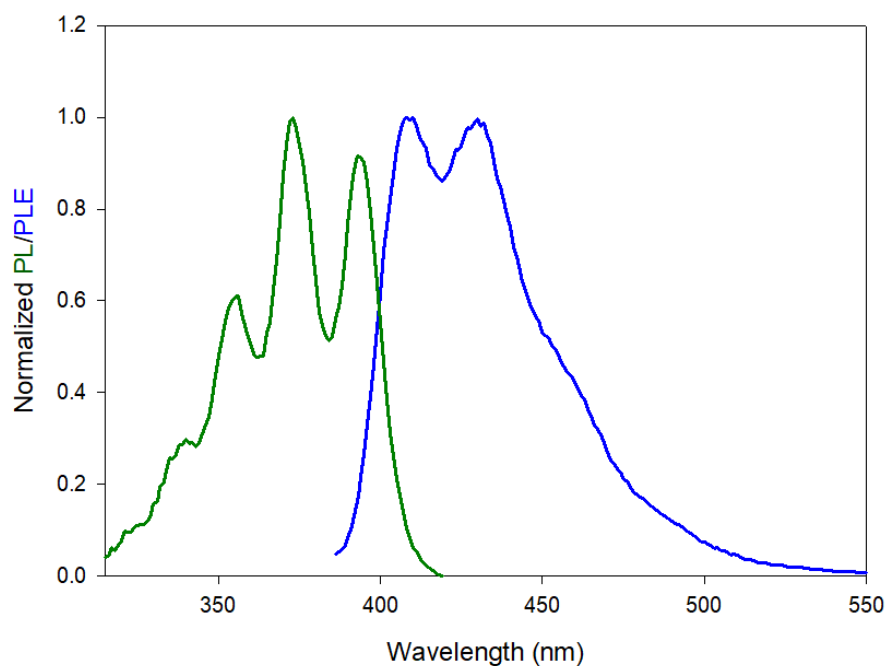


Figure 4.4 PL and PL excitation spectra of a DPA:THF solution.

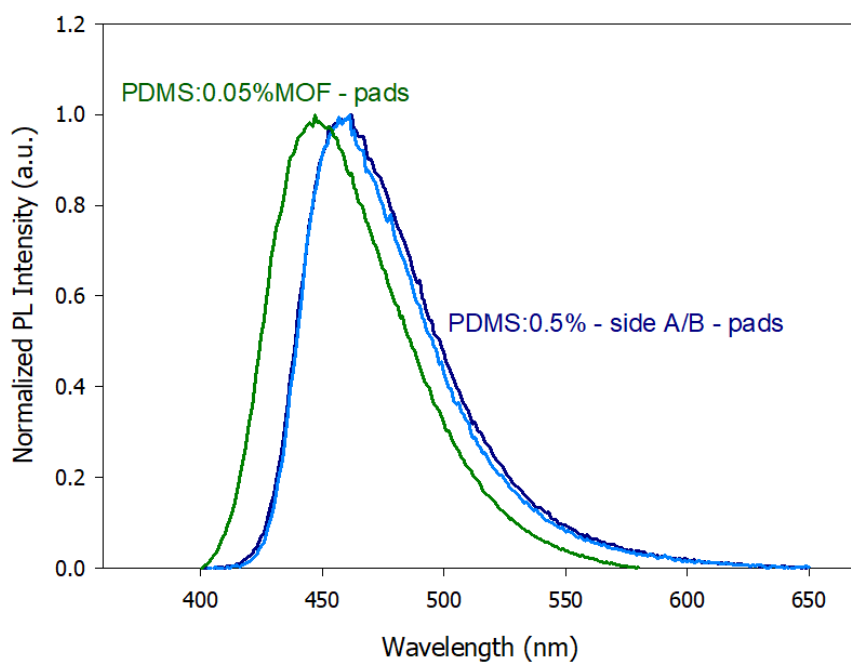


Figure 4.5 Photoluminescence spectra of PDMS pad with concentration of MOF, 0.05% (green) and 0.5%. For the latter, the spectra for both sides of the pad are illustrated (dark and light blue).

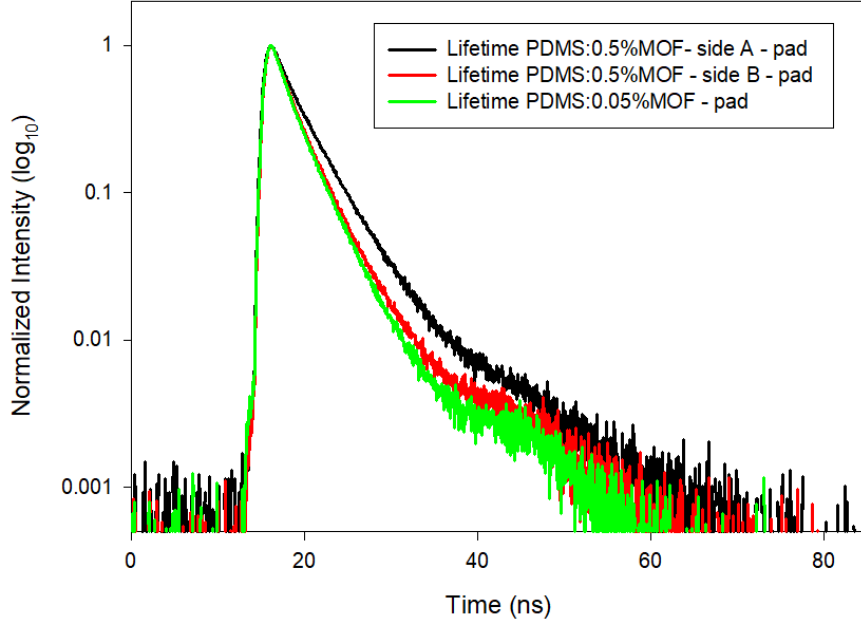


Figure 4.6 Time resolved PL spectra of PDMS pad with concentration of MOF, 0.05% and 0.5%. For the latter, the spectra for both sides of the pad are shown.

of the instrument response function (IRF) once is reduced to $\sim 5\%$ has been considered.

$$f(t) = \sum_{i=1}^2 a_i e^{-(t/\tau_i)} \quad (4.1)$$

The average decay time, which describes the decay behavior of the PL pulse, was calculated through the Eq. 1.10 and using the fit results. Note that in the Eq. 1.10 the weights correspond to ρ_i but the ones obtained from the fit are a_i .

To understand the emission behavior of the three rod-like samples, 3 D contour plots illustrated in Fig. 4.7 have been analyzed. It begins to appreciate a very different dynamic over time between the sample with low concentration and the two with the highest one. Furthermore, the peak emission of the PMMA:2.5% MOF shifts towards greater wavelengths with time.

Indeed, the emission at different time intervals of the PMMA:0.1% MOF does not change (see Fig. 4.8a). The yellow curve represents the PL emission over the time range from 0 ns to 20 ns. The PL dynamic, which is illustrated in Fig. 4.8b has a decay in agreement with a single exponential decay function ($f(t) = y_0 + a_1 e^{-t/\tau_1}$). Its lifetime has resulted equal to 5.5 ns. Then, knowing that the lifetime of the DPA molecule is around 6.9 ns, the quantum yield of this sample resulted equal to $\sim 80\%$.

For the higher concentrated samples the spectra change with the time (see Fig. 4.9a and Fig. 4.10a). In particular, the emission intensities of the PMMA:0.5% MOF increase at greater wavelengths, while the overall emission spectra of the PMMA:2.5% MOF shift toward the red region.

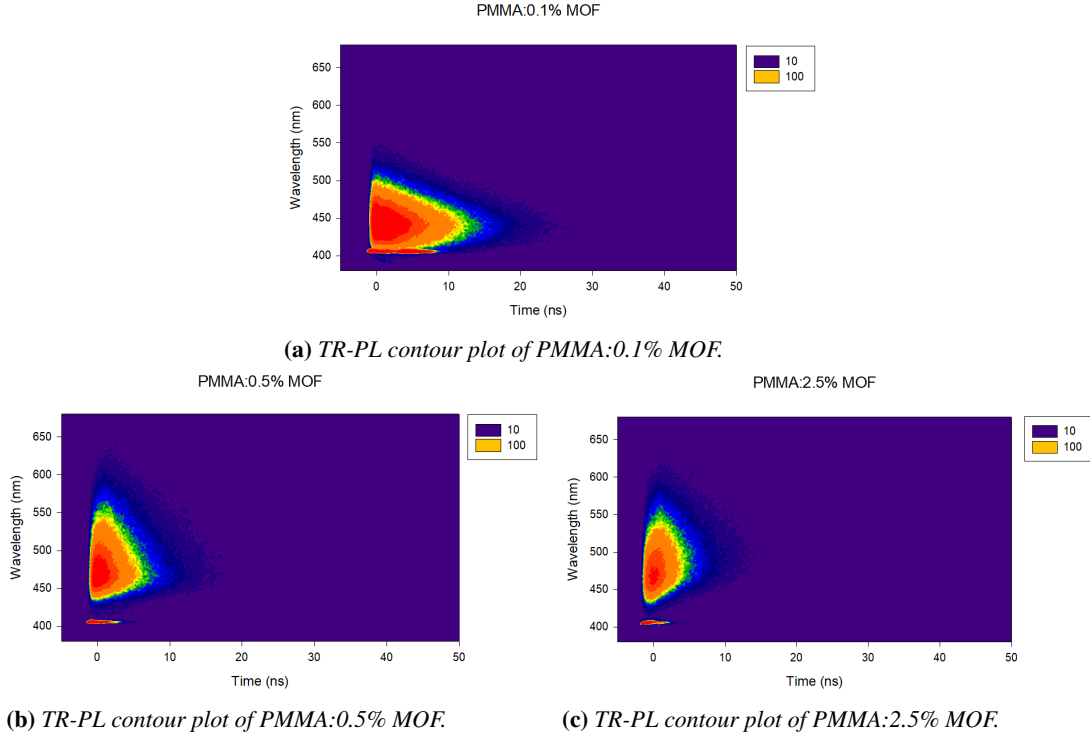


Figure 4.7 TR-PL contour plots of the three tested rod-like samples.

A proof that more components are present during their emission could be given from the lifetime calculation. Both samples at the highest concentration have a decay in agreement with a fit function having two exponential decay components and a background (y_0):

$$f(t) = y_0 + \sum_{i=1}^2 a_i e^{-(t/\tau_i)} \quad (4.2)$$

Also for these two nanocomposites the average decay ($\tau_{d;av}^{PL}$) time has been calculated with the same approach used for the pad-like samples. Then, $\tau_{d;av}^{PL}$ resulted equal to 3.8 ns and 2.9 ns, for the PMMA:0.5% MOF and PMMA:2.5% MOF respectively. Further analysis has been done about the latter nanocomposite to understand the behavior of the two emission components. The study has been done taking into account the lifetime over the wavelength range 420-450 nm (component A) and 550-600 nm (component B) to have better discrimination of the behavior about the blue component (A) and the more red-shifted one (B), respectively. Therefore, using the same fit function, $\tau_{d;av}^{PL}$ has been calculated and it is resulted equal to 2.3 ns for the first, and 4.9 ns for the latter. Their dynamic is illustrated in Fig. 4.11.

The emission wavelengths, the fit results, and the PL average decay times ($\tau_{d;av}^{PL}$) of the tested pad-like and rod-like nanocomposites are reported in Tab. 4.1.

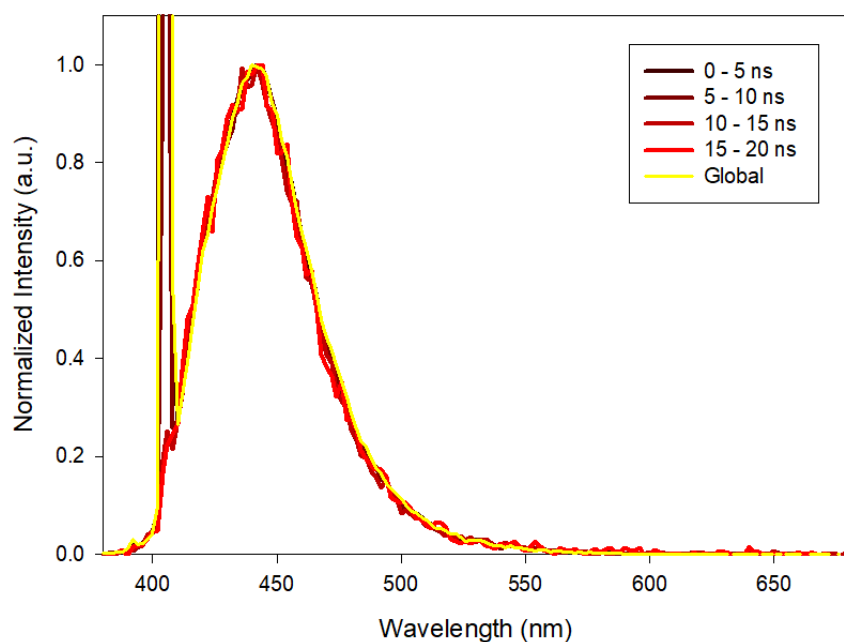
		λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	a_1 (%)	a_2 (%)	$\tau_{d;av}^{PL}$ (ns)
DPA:THF		405	—	—	—	—	—
		430	—	—	—	—	—
PDMS:0.05% MOF		445	4.0	1.8	44	56	2.8
PDMS:0.5% MOF	side A	460	5.4	2.4	42	58	3.7
	side B	460	4.8	2.0	35	65	2.9
PMMA:0.1% MOF		442	5.5	—	100	—	5.5
PMMA:0.5% MOF		470	2.2	5.9	57	43	3.8
PMMA:2.5% MOF	Global	472	2.4	4.4	78	22	2.9
	Comp. A	—	1.5	5.1	79	21	2.3
	Comp. B	—	4.1	11.8	90	10	4.9

Table 4.1 Wavelength emission, fit results and average decay time of the TR-PL spectra about PDMS pads and PMMA rods nanocomposites. Results of the two sides (A and B) of PDMS:0.5% MOF and those of the two emission components (A and B) of PMMA:2.5% MOF are reported. Furthermore, the emission wavelengths of DPA:THF are reported. An error in the range of 2% has been estimated about the fit results and the average decay time.

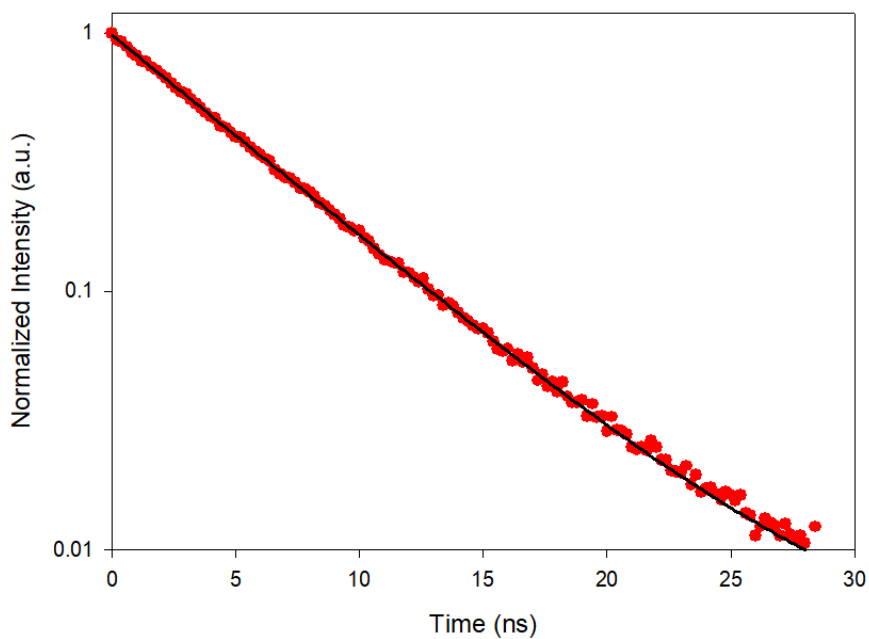
4.1.3 Discussion

As it can be seen in Fig. 4.5, the PL spectra about pad-like PDMS:0.5% MOF are shifted of 15 nm with respect to the PDMS:0.05% MOF. A slight red-shift is expected since MOFs can be larger in size as concentration increases. The PL emissions between the two sides of the PDMS:0.5% MOF pad have a negligible difference, however, their average decay time has not it. An explanation of these PL and TR-PL behaviour of the PDMS:0.5% MOF could be due to the spot of the light source. The light beam is narrower in TR-PL measurements than the PL ones, then more or less large aggregates can be hit by the light beam, or not, with more probability. Such as, for the side A, larger aggregates could be hit by the laser beam.

The emission of the PMMA:0.1% MOF has resulted the same at different decay time intervals and its PL dynamic has a monoexponential behavior. This means that the MOFs are well dispersed into the matrix and that there is just a population of emitters. Indeed, the average decay time is almost as that of the single DPA molecule. Therefore with this sample, the quantum yield was almost maximized. Increasing the concentration of the nanocomposites the overall emission spectra of the PMMA:0.5% MOF and PMMA:2.5% MOF are shifted toward greater wavelengths with respect to the PMMA:0.1% MOF spectrum. Furthermore, their emissions change with time (delay PL) and their decay has a multiexponential behavior with a $\tau_{d;av}^{PL}$ shorter than the lower concentrated nanocomposite. This could be due to some non-ideal passivation and possible aggregation quenching. Proof of this, the further analysis which has been performed taking into consideration two different emission regions of the PMMA:2.5% MOF. It saw that the blue component has a $\tau_{d;av}^{PL}$ lower than the red-shifted one. This suggests that the population of the second acts as a quencher for the first.

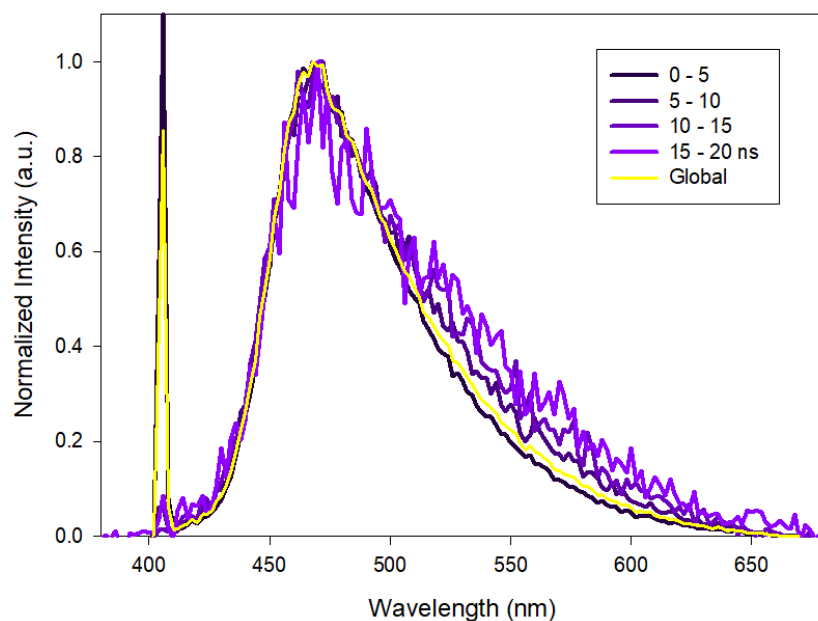


(a) PL spectra of the rod-like PMMA:0.1% MOF at different time intervals. The yellow curve correspond to PL spectra taken integrating on the overall time scale.

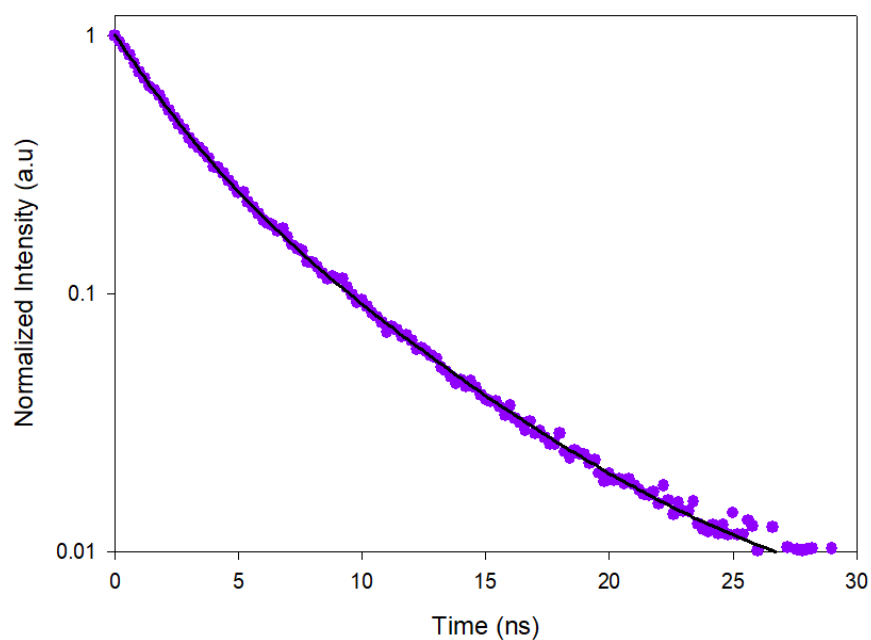


(b) TR-PL spectrum of the rod-like PMMA:0.1% MOF (red dot) with the fit (black line).

Figure 4.8 PL and TR-PL spectra of the rod-like PMMA:0.1% MOF.

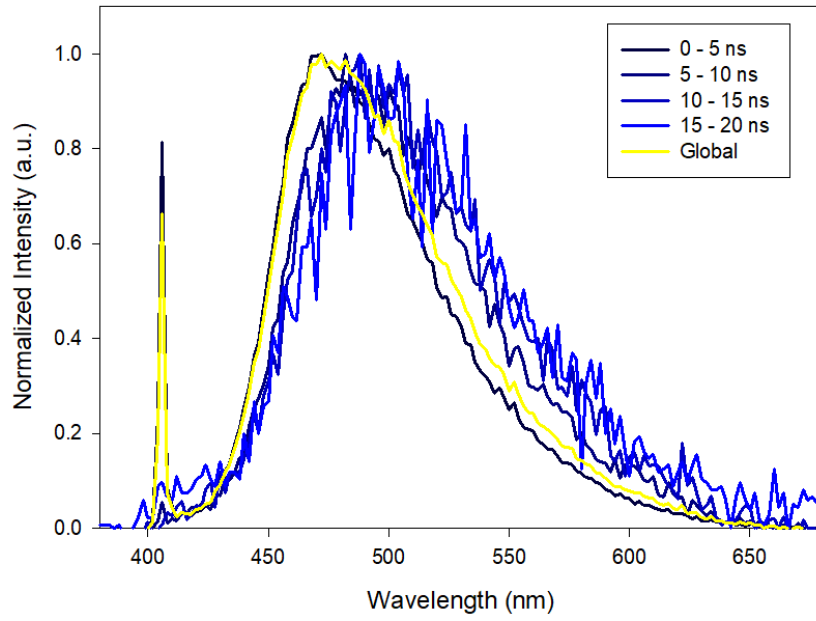


(a) PL spectra of the rod-like PMMA:0.5% MOF at different time intervals. The yellow curve correspond to PL spectra taken integrating on the overall time scale.

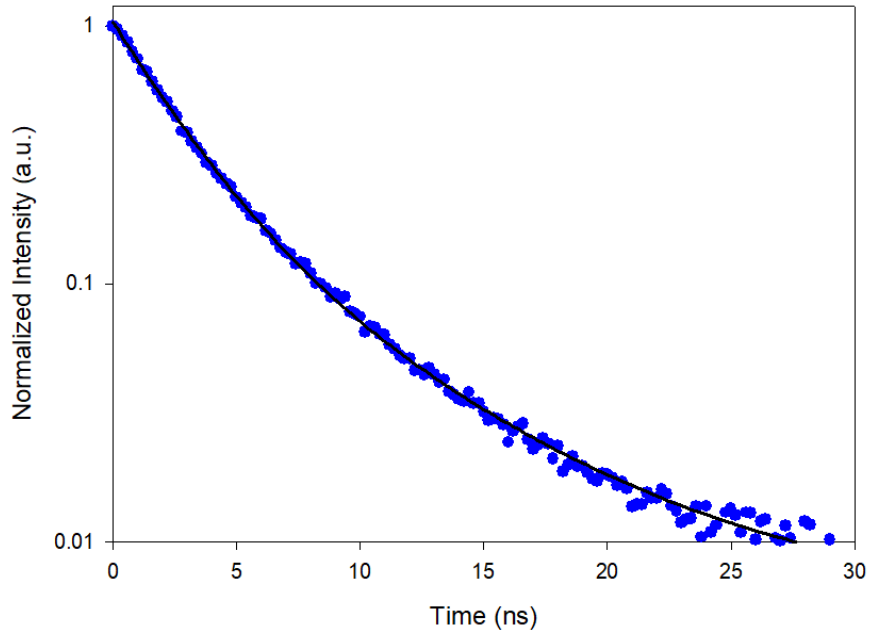


(b) TR-PL spectrum of the rod-like PMMA:0.5% MOF (purple dot) with the fit (black line).

Figure 4.9 PL and TR-PL spectra of the rod-like PMMA:0.5% MOF.



(a) PL spectra of the rod-like PMMA:2.5% MOF at different time intervals. The yellow curve correspond to PL spectra taken integrating on the overall time scale.



(b) TR-PL spectrum of the rod-like PMMA:2.5% MOF (blue dot) with the fit (black line).

Figure 4.10 PL and TR-PL spectra of the rod-like PMMA:2.5% MOF.

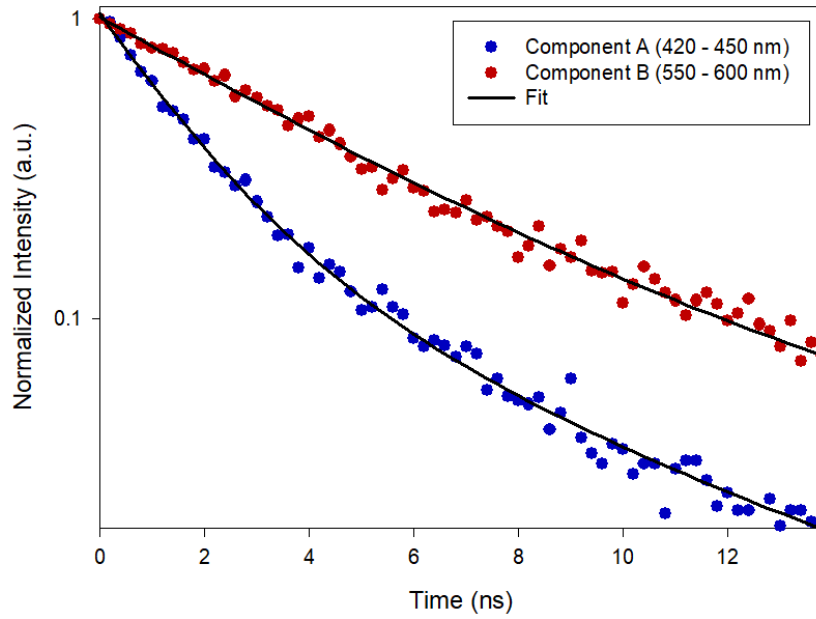


Figure 4.11 TR-PL of two emission components about rod-like PMMA:2.5% MOF (dots) and their fit (black lines).

Radiativeless mechanisms short the emission decay and then the quantum yield. However, to have good scintillators and have an efficient radiation matter interaction, nanocomposites with high concentration are needed. Then, a compromise must be found with the quantum yield and a good scintillation response.

4.2 Light yield

The light measurements have been performed with two systems that can support distinct photodetectors. In the following section, light yield results using a PMT and a SiPM are presented.

4.2.1 Materials and methods

Photomultiplier tube as photodetector

The light yield measurement of nanocomposite samples has been performed with a Hamamatsu R2059 PMT connected to a DT5720A CAEN digitizer which performs charge integration in ADC units.

To determine the intrinsic light yield of the tested nanocomposites, the signal produced by them with different gamma sources was compared with the one of the single photoelectron peak. The sample signals were acquired by placing the nanocomposite on the PMT window, and the source close to it (see Fig. 4.12a). To measure the single photoelectron signals, instead, samples

and sources have been removed from the PMT. The latter has been covered with a cap to shield it from eventual residual light in the bench.

Silicon photomultiplier as photodetector

The light yield upon gamma irradiation has been also measured using several gamma sources in order to investigate the LY at different gamma energies, in particular, the range of energies used was 122-1332 keV. Especially, as in the paragraph 4.2.2 is reported, more detailed analysis have been done using the ^{137}Cs (662 keV).

Each nanocomposite has been coupled with an Hamamatsu S13360-3050CS SiPM (Fig 4.12b). The latter was biased with 61 V and the signals generated by the SiPM were readout by a Tele-dyne Lecroy HD4096 oscilloscope. For this setup, the trigger position can be chosen more precisely and it has been set at 30 mV to avoid the SiPM noise arising from dark count rates or gamma interaction with the SiPM epoxy window. This has been validated measuring with the detector and the source only. Indeed, a negligible number of events have been recorded.

The integral of the pulse signal corresponds to the amount of charge produced in the SiPM because of photons detected. Therefore, for each sample, a histogram of the amount of charge normalized for the total number of the events has been recorded and compared with that of a BGO crystal.

4.2.2 Results

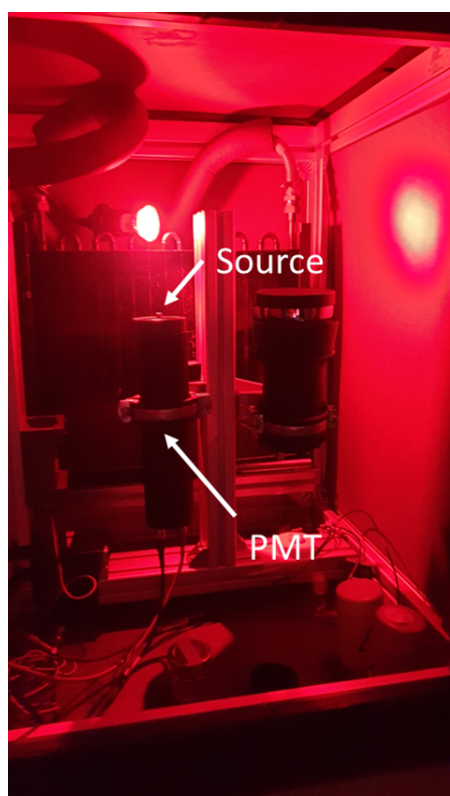
Photomultiplier tube as photodetector

The first samples investigated were the pads ($10 \times 5 \text{ mm}^2$) of PDMS and PMMA. They have been coupled with the PMT through some optical grease and ^{137}Cs source has been used. Their LY curves are in Fig. 4.13.

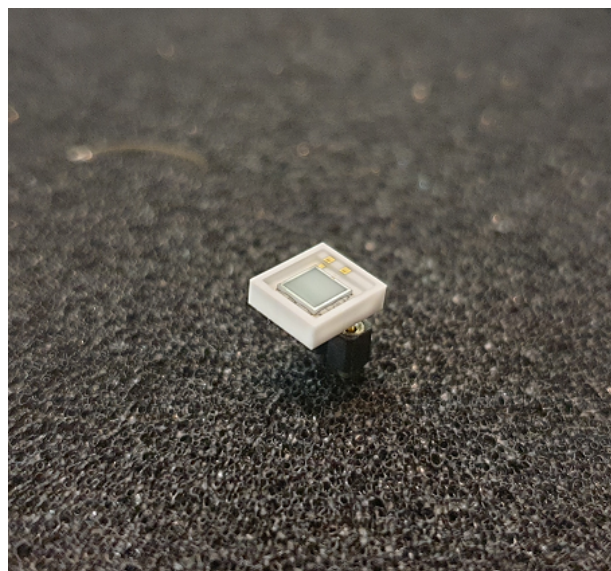
Other measurements have been done using ^{55}Fe source (6 keV). They have been performed on nanocomposites with plates and pixels ($2 \times 2 \times 3 \text{ mm}^3$) geometries which are obtained by cutting the pads in the Lab 27 at CERN. The measured pixels were only those of PDMS:0.5% MOF and PMMA:0.5% MOF and they have been wrapped in teflon (used as a reflector) and coupled to the detector with some optical grease to maximize the light extraction. In Fig. 4.14 and Fig. 4.15 no difference of nanocomposite signals with respect to sole Cs source can be seen. An explanation could be that the weighted QE is simply too low to detect more than few photons, and the PMT is not able to resolve single photons.

Silicon photomultiplier as photodetector

In the first analysis to understand the behavior of the number of photons emitted through the scintillation process, measurements about the square pixels of PMMA:0.5% MOF with different radiation energies have been performed. The sources used were ^{137}Cs (662 keV), ^{22}Na (511 keV), ^{57}Co (122 keV), and ^{60}Co (1173 keV and 1332 keV). The sample has been wrapped in a reflector and coupled with the SiPM through a non-scintillating optical coupling agent (Meltmount, $n=1.662$). The light yield curves are illustrated in Fig. 4.16.



(a) Experimental setup with the PMT used to study the light yield.



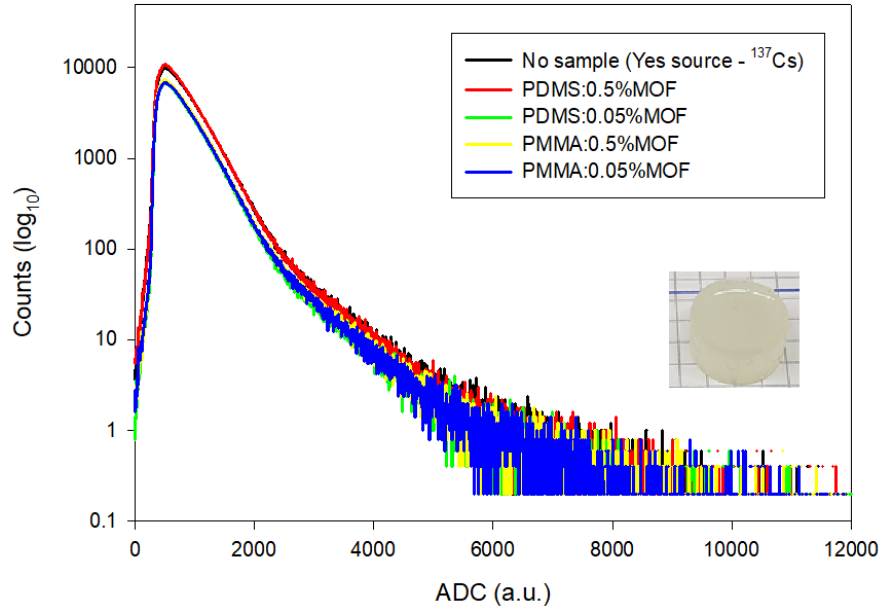
(b) Hamamatsu S13360-3050CS SiPM used for a further method to study the light yield.

Figure 4.12 Experimental setup with the photomultiplier tube and SiPM used to study the light yield.

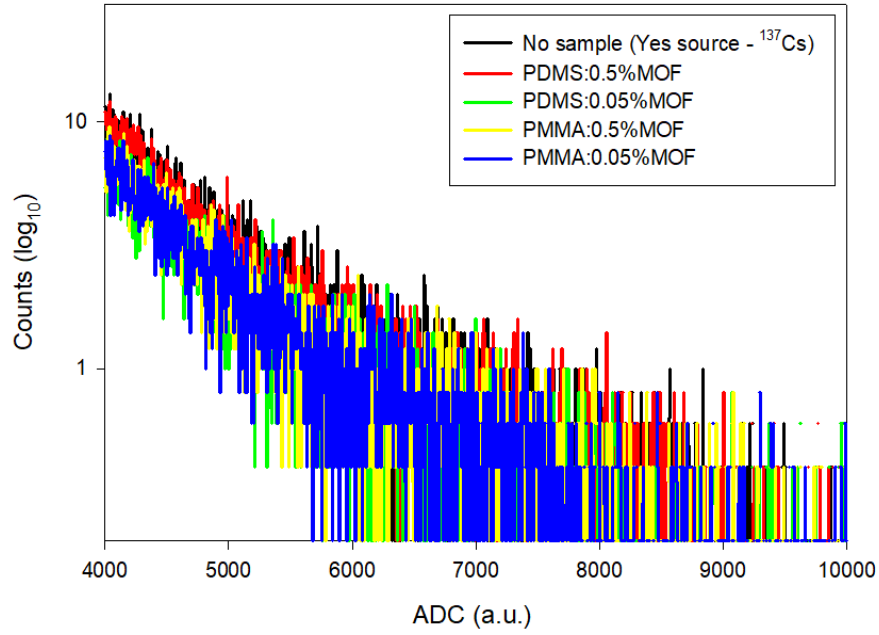
Subsequently, the LY of square pixels of PMMA:0.05% MOF, PDMS:0.5% MOF, and PDMS:0.05% MOF have been investigated with the same reflector and Meltmount but using cesium source only. These studies are shown in Fig. 4.17 and it can be seen that the curves appear superimposed. The reason could be the scintillation of the teflon used to wrap the samples. Therefore, its signal was compared together to the sample ones and is reported as an inset of the Fig. 4.17.

A solution could be to not use the teflon sacrificing part of the benefit that the reflector brings to the extraction of light to be sure that the acquired signal is the one of the samples. Then the PMMA polymer-based nanocomposites were studied without teflon wrapping and using the cesium source. In particular, the square pixel of PMMA:0.05% MOF, and those cylindrical of PMMA:0.5% MOF and PMMA:2.5% MOF.

No distinct photopeak is visible, however, based on the effective atomic number it is expected that the maximum deposited energy is coming from the Compton edge, eg. for ^{137}Cs 478 keV. Their plots in Fig. 4.18 do not show any photopeak. Then to extrapolate the LY values a calibration with a known inorganic crystal has been performed. In this case, was used a pixel $2 \times 2 \times 3 \text{ mm}^3$ of BGO and the number of detected photons in the BGO case has been

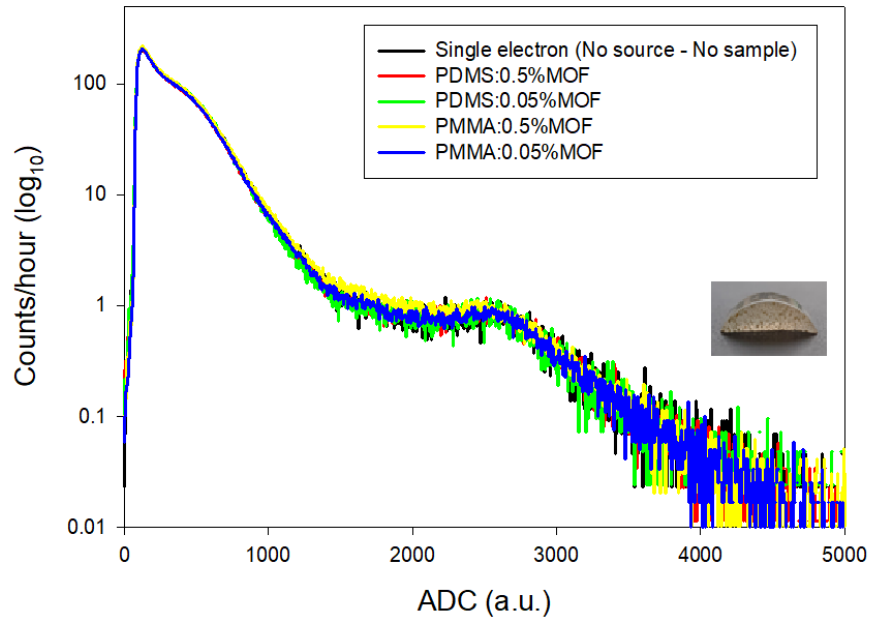


(a) Light yield signal of the nanocomposites in pad geometry acquired using ^{137}Cs source.

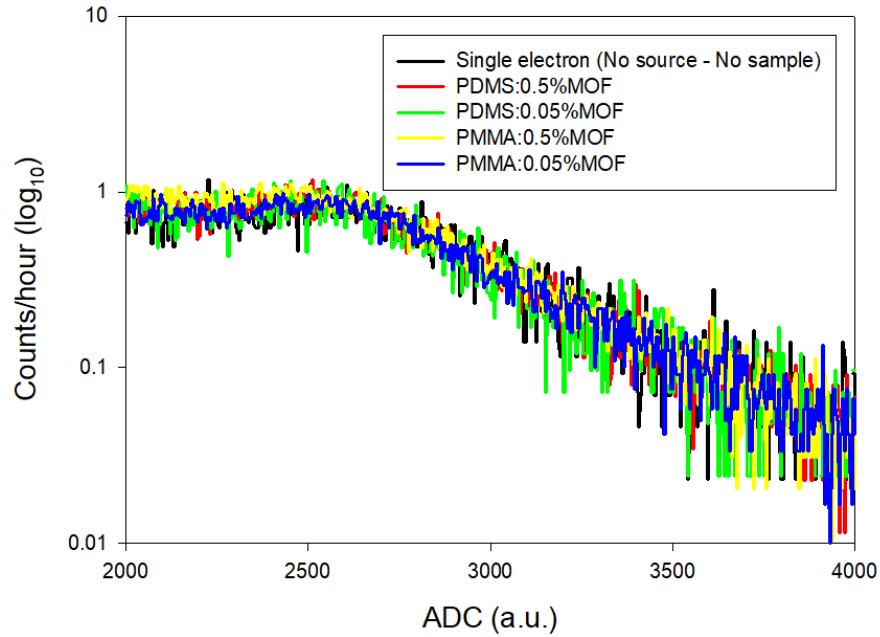


(b) Zoom of the tails about LY signals of the nanocomposites in pad geometries.

Figure 4.13 Light yield signals about nanocomposites in pad geometry acquired using ^{137}Cs source. A zoom of the signals is reported for a better comparison.

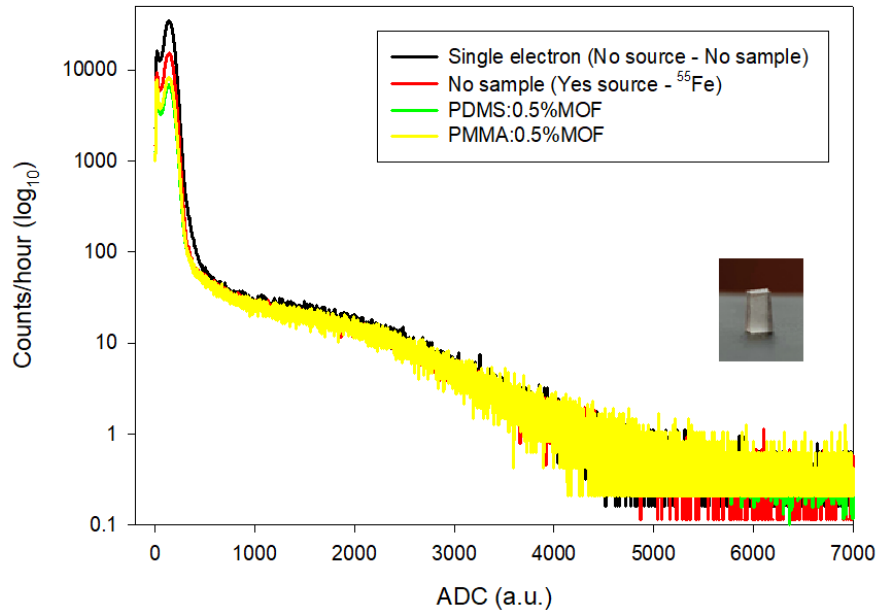


(a) Light yield curves of the plate nanocomposites.

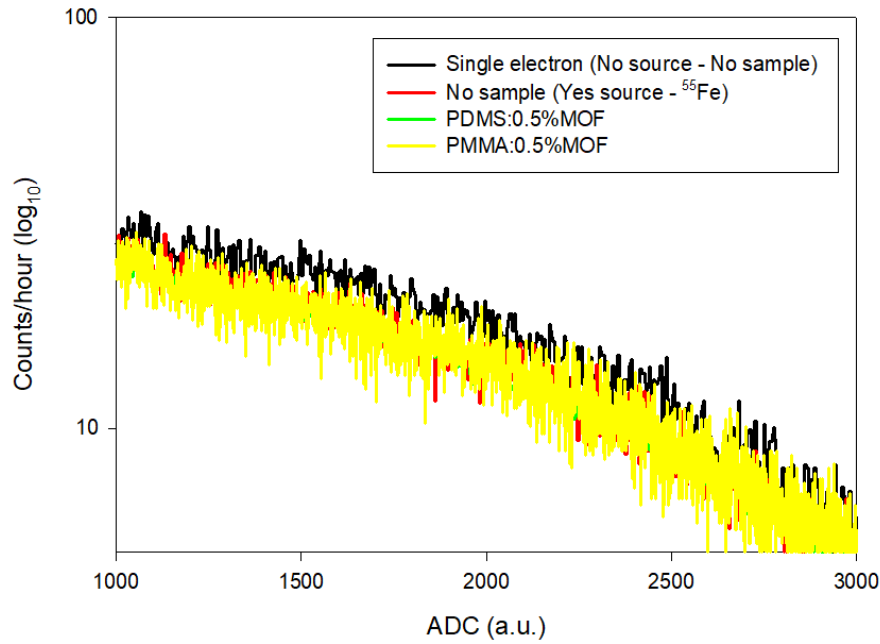


(b) Zoom of the light yield curves of the plate nanocomposites.

Figure 4.14 Light yield curves about nanocomposites in plate geometries obtained by cutting the relative pad-like samples. The curves have been acquired using ^{55}Fe source. The signal "No source - No sample" corresponds to the single electron one. A zoom of their signals is reported.



(a) Light yield curves of the pixel nanocomposites.



(b) Zoom of the light yield curves of the pixel nanocomposites.

Figure 4.15 Light yield curves about nanocomposites in pixel geometries obtained by cutting the relative pad-like samples. The curves have been acquired using ^{55}Fe source. The signal "No source - No sample" corresponds to the single electron one. A zoom of their signals is reported.

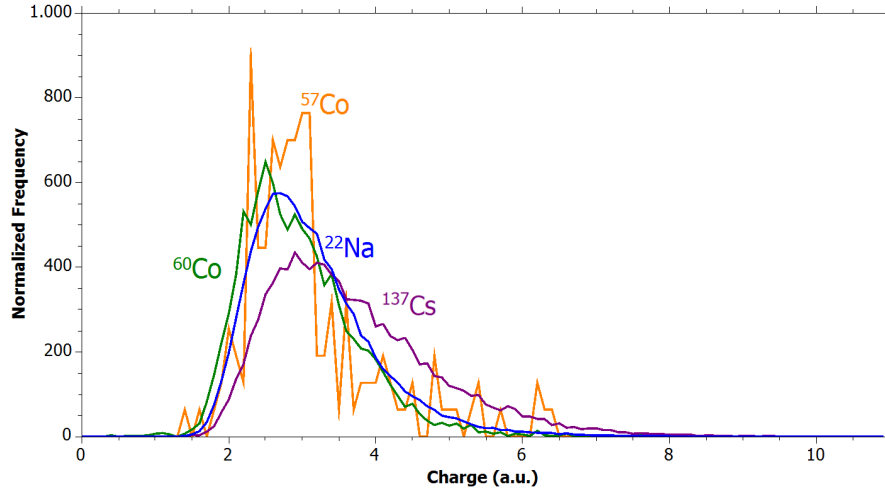


Figure 4.16 Light yield curves about square pixel of PMMA:0.5% MOF studied with different sources.

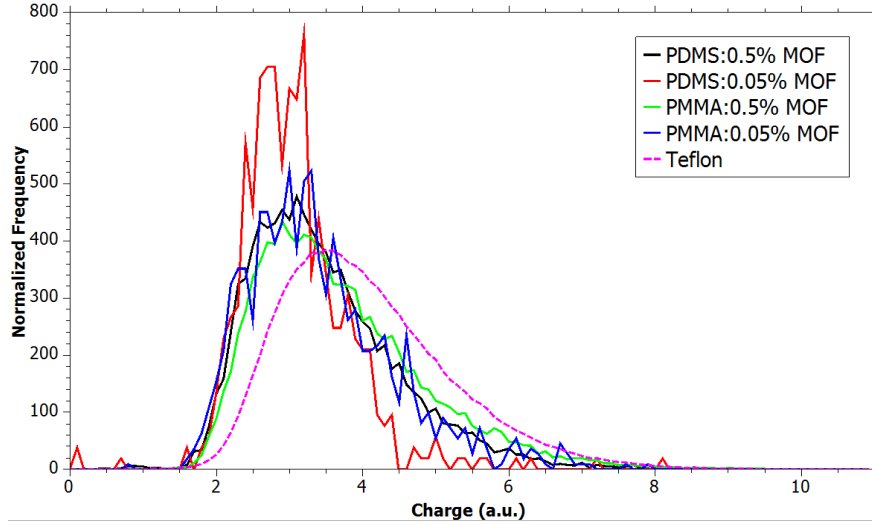


Figure 4.17 Light yield curves about square pixels based on PDMS and PMMA polymers. Also the teflon signal was reported for comparison.

extrapolated using the Eq. 1.12 and resulted to be equal to 2000 (10% error has been estimated).

This was possible since the weighted photo detection efficiency ($\langle \text{PDE} \rangle$) has been calculated with the Eq. 4.3, using the BGO emission spectra (provided by the CERN research group) and the $\langle \text{PDE} \rangle$ of the SiPM used which resulted to be equal 50% (an error of 4% was estimated). As LTE and ILY values it has been used those present in the work [12], which are 10.7 ph/keV and 58% respectively; while as deposited energy it has been considered 662 keV because the BGO photopeak, which is at 30 a.u., has been treated for the calibration. Consequently, 1 a.u. corresponds to 68 photons.

	Compton edge position (a.u.)	#detected photons	<PDE> (%)
PMMA:0.05% MOF	3.5	238	54
PMMA:0.5% MOF	4	272	51
PMMA:2.5% MOF	4.3	292	50

Table 4.2 Compton edge position, the corresponding number of photons for each tested unwrapped sample, and their weighted PDE. The Compton edge position error and that of the number of detected photons are in the range of 30%. The weighted PDE error it assumed to be in range of 5%.

$$\langle PDE \rangle = \frac{\int PL(\lambda) \cdot PDE(\lambda) d\lambda}{\int PL(\lambda) d\lambda} \quad (4.3)$$

To define with certainty the energy deposited in the sample the position of the Compton edge had to be estimated. However, the error on the estimation could in the range of 30% . The Compton edge position and the corresponding number of photons are listed in Tab. 4.2 for each sample.

Since ^{137}Cs (662 keV) has been used, then the maximum amount of the deposited energy (E) at the Compton edge was ~ 478 keV and has been calculated with the following formula deriving from the 1.7:

$$E = E_\gamma - \frac{E_\gamma}{1 + \frac{2E_\gamma}{m_0c^2}} \quad (4.4)$$

Then, for each sample, it was possible to calculate the LY with respect to that of the BGO crystal. To get the ILY of the nanocomposites, first of all, the weighted PDE has been calculated using the sample emission spectra and the PDE of the used SiPM, then has been made the rough assumption that their LTE was comparable to that of plastic BC-422 (74%, [12]).

For each sample the weighted PDEs are reported in Tab. 4.2 while the ILY in Tab. 4.3.

A second test was performed to know if the LY signal of the Fig. 4.18 was that of the samples. Then, the signal of the SiPM with Metlmount and PMMA matrix (blank sample) one has been studied and their rate of events as reported with that of the analysed samples in Tab. 4.3.

4.2.3 Discussion

The plot of the Fig. 4.13 does not show any photo photopeak for all samples. This could be due to the lower cross-section of the photoelectric interaction with respect to the Compton effect one, since the effective atomic number of the absorber is not above 40 and the gamma energy hits the samples was 662 keV (see Fig. 1.1). Furthermore, the calculation of the LY was not possible since all sample curves are equivalent to that without a sample. Therefore it has been used ^{55}Fe source to increase the photoelectric interaction probability. Besides using a weaker source, the size of the samples was reduced in order to minimize the inner light scattering. Nevertheless, the curves are equal to that of the single electron as see in Fig 4.14 and Fig 4.15. Then, due

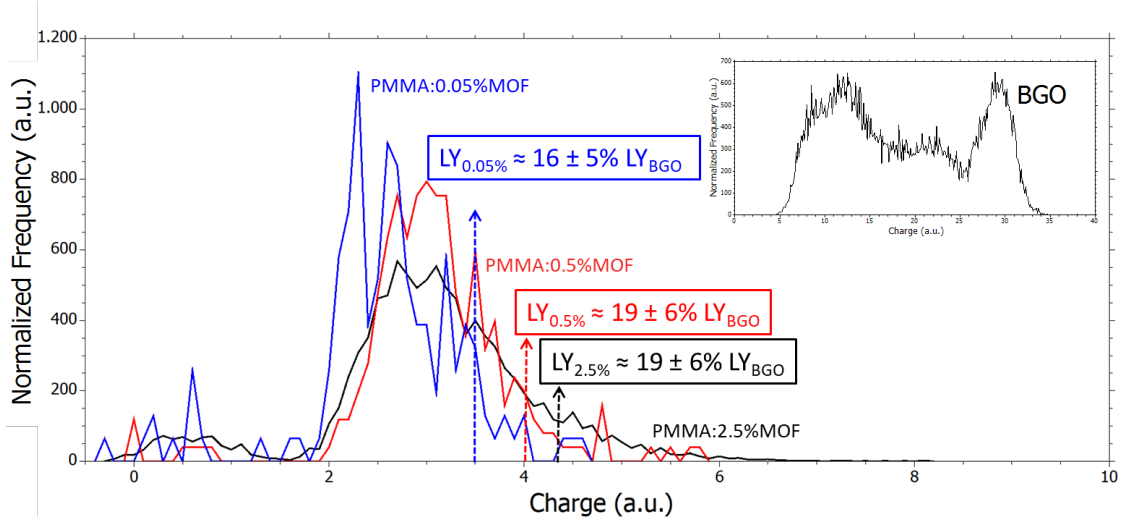


Figure 4.18 Light yield curves of unwrapped PMMA polymer-based pixel nanocomposites. In the inset is reported the light yield curve of the BGO reference crystal. The dashed arrow positions have been estimated to be the Compton edge for each sample.

	Rate (#events/h)	LY_{MOF}/LY_{BGO} (%)	ILY (ph/keV)
SiPM	0.3	—	—
PMMA matrix	0.5	—	—
PMMA:0.05% MOF	2	16	1.2
PMMA:0.5% MOF	14	19	1.6
PMMA:2.5% MOF	510	19	1.6
BGO	—	—	10.7

Table 4.3 Light yield of three pixel PMMA nanocomposite. The PMMA:0.05% MOF nanocomposite is in square pixel geometry. The error of the LY ratio and that of ILY about nanocomposites is in the range of 30%. The ILY of BGO pixel has been taken from [12] and its error was estimated to be 10%.

to the weak radiation matter interaction and feasible light losses, the PMT could have been not sensitive enough to distinguish the few photons arriving on it. A most sensitive photodetector has been used, the SiPM aforementioned.

As it can be seen from Fig. 4.16 varying the source no significant change in the signal position appears. Indeed, once the signal of the teflon reflector has been analysed it has been noticed that it is dominant with respect to those of the wrapped nanocomposites (Fig. 4.16). The shift of the teflon signal with respect to that of the nanocomposites could be due to the fluctuation of the amount of the crosstalk in the SiPM.

The rate of events reported in Tab. 4.3 prove that the SiPM and, in particular, the PMMA matrix does not interact significantly with the ionizing radiation, indeed the few events recorded did not allow to recreate any LY curve. Moreover, the rate increase considerably with increasing

the concentration of the nanocomposites, however, the detected light is about 5 times lower than in BGO. This could be due to a lower ILY than BGO one and a partial self-absorption affecting the nanocomposite.

4.3 Rise and decay time

4.3.1 Materials and methods

The nanocomposites for which the dynamic of scintillation has been studied were the rods of PMMA:0.1%MOF, PMMA:0.5%MOF, and PMMA:2.5%MOF. In order to investigate the scintillation response, a pulsed X-ray excitation source was used and the light was detected by a hybrid photomultiplier tube. The X-ray excitation was a light excited Hamamatsu X-ray Tube (XRT) N5084 which consists of a photocathode, a Tungsten target, and a Beryllium window. The XRT is connected to an ultra-short pulsed laser, a Picosecond Pulsed Diode Laser (PicoQuant PDL 800), with a variable repetition rate which can go up to 5 MHz, wavelength range between 255–600 nm and a Gaussian Impulse Response Function (IRF) with $\sigma = 54$ ps. The pulsed light acts as input excitation light, which is converted into an electron beam at the photocathode. The beam is then accelerated and focused by electron lenses on the Tungsten target where it collides, producing pulse bremsstrahlung radiation and characteristic X-rays, according to the time profile of the laser. X-rays are emitted through a Beryllium window of 250 μm of thickness, which allows minimizing the X-ray attenuation by the XRT envelope. The X-ray energy spectrum is defined by maximum operating voltage (40 kV), then is a bremsstrahlung continuous spectrum extending up to 40 keV but having a peak around 9 keV due to Tungsten L-characteristic X-ray photons. A collimator is placed a few millimeters in front of the Beryllium window and, just beyond it, the sample is placed on a sample holder. The light emitted by the sample is detected by a Hybrid PMT Becker&Hickl HPM-100-07 operating in time-correlated single-photon counting (TCSPC) mode measuring the photon arrival time delay with respect to the laser excitation pulse. The wavelength range of the HPMT spans from 220 to 850 nm and a peak detection quantum efficiency of $\sim 22\%$ at 400 nm.

The output of the HPMT is read out and triggered (after an amplification stage) by a time-to-digital converter Cronologic xTDC4 with a time resolution of 8 ps.

Experimentally, the samples have been studied placing them, relative to the XRT and the HPMT, in order to collect the emission light in reflection mode. This has the advantage to separate the emission light from the excitation one since the former is isotropically emitted while the latter is partially transmitted through the medium. The repetition rate of the laser has been set to 1 MHz.

The nanocomposites for which the scintillation dynamic was studied were the PMMA-based rods with concentrations 0.1%, 0.5% and, 2.5% of MOF. A bandpass filter of 450 ± 20 nm FWHM by Thorlabs has been used screwed to the Hybrid PMT window to shield any laser reflections when the PMMA:0.1% MOF was tested. For the other two samples, having a peak emission more towards the red, a bandpass filter of 500 ± 20 nm FWHM has been used.

Since the amplifier acts also as a signal discriminator then a threshold of ~ 130 mV has

been applied in order to improve the SNR. This threshold value has been used to study the PMMA:0.1% MOF and PMMA:0.5% MOF, while a threshold of ~ 120 mV has been set for the PMMA:2.5% MOF.

In Fig. 4.19 is illustrated a scheme of the experimental setup aforementioned in the configuration used to study the scintillation dynamic of the nanocomposite and a picture of the used Hybrid PMT. The picture of the experimental setup (Fig. 4.19b) was taken without a bandpass filter.

A general describing model for the description of the overall behavior of the pulse scintillation can be that in Eq. 1.9. However, before to extrapolate the parameter of interest the scintillation rate must be deconvoluted from the IRF of the experimental setup which affects the scintillation pulse. The laser IRF is well modeled by a Gaussian function:

$$g(t)_{laser} = \frac{1}{\sigma_{IRF}\sqrt{2\pi}} \exp\left[-\frac{t^2}{2\sigma_{IRF}^2}\right] \quad (4.5)$$

Instead, the XRT N5084 IRF can be modeled as studied in previous works [35] [36], with an asymmetric function with a first exponential rising component (τ_{xr}) and a second exponential decay one (τ_{xd}):

$$g(t)_{XRT} = \begin{cases} \frac{1}{e^{\theta/\tau_{xr}}} e^{t/\tau_{xr}}, & t \leq \theta \\ e^{(\theta-t)/\tau_{xd}}, & t > \theta \end{cases} \quad (4.6)$$

Therefore, the fit function used to extrapolate the rise and decay time of the three nanocomposites was the convolution between Eq. 1.9, Eq. 4.5 and Eq. 4.6.

Due to the asymmetry of the XRT IRF, this convolution integral can not be solved analytically. It was therefore numerically calculated using the RooFit package, which employs the Fast Fourier Transform algorithm. To speed up the fit procedure, for each of these parameters a lower and upper limit was set, and in this range, they were free to vary. On the contrary, the parameters related to IRF were fixed on the basis of previous studies [36], in particular: $\sigma_{IRF} = 54$ ps (experimentally measured), $\tau_{xr} = 20$ ps and $\tau_{xd} = 50$ ps (defined using the FWHM information of the XRT specification).

4.3.2 Results

The scintillation dynamic of the three rod-like nanocomposites resulted to be in agreement with a fit function having three exponential decay components (Eq. 4.7), which derives from the Eq. 1.9.

$$f(t) = \Theta(t) \sum_{i=1}^3 \frac{e^{-(t/\tau_{d,i})} - e^{-(t/\tau_{r,1})}}{\tau_{d,i} - \tau_{r,1}} \rho_i \quad (4.7)$$

Using the fit results both the effective decay time ($\tau_{d;eff}$) and the average decay time ($\tau_{d;av}^{SC}$) have been calculated for each tested nanocomposite. The first is useful in timing applications because it gives more importance to the fast components and is related to the initial photon-time density (IPTD), thus it carries the information about the intrinsic timing capabilities of the

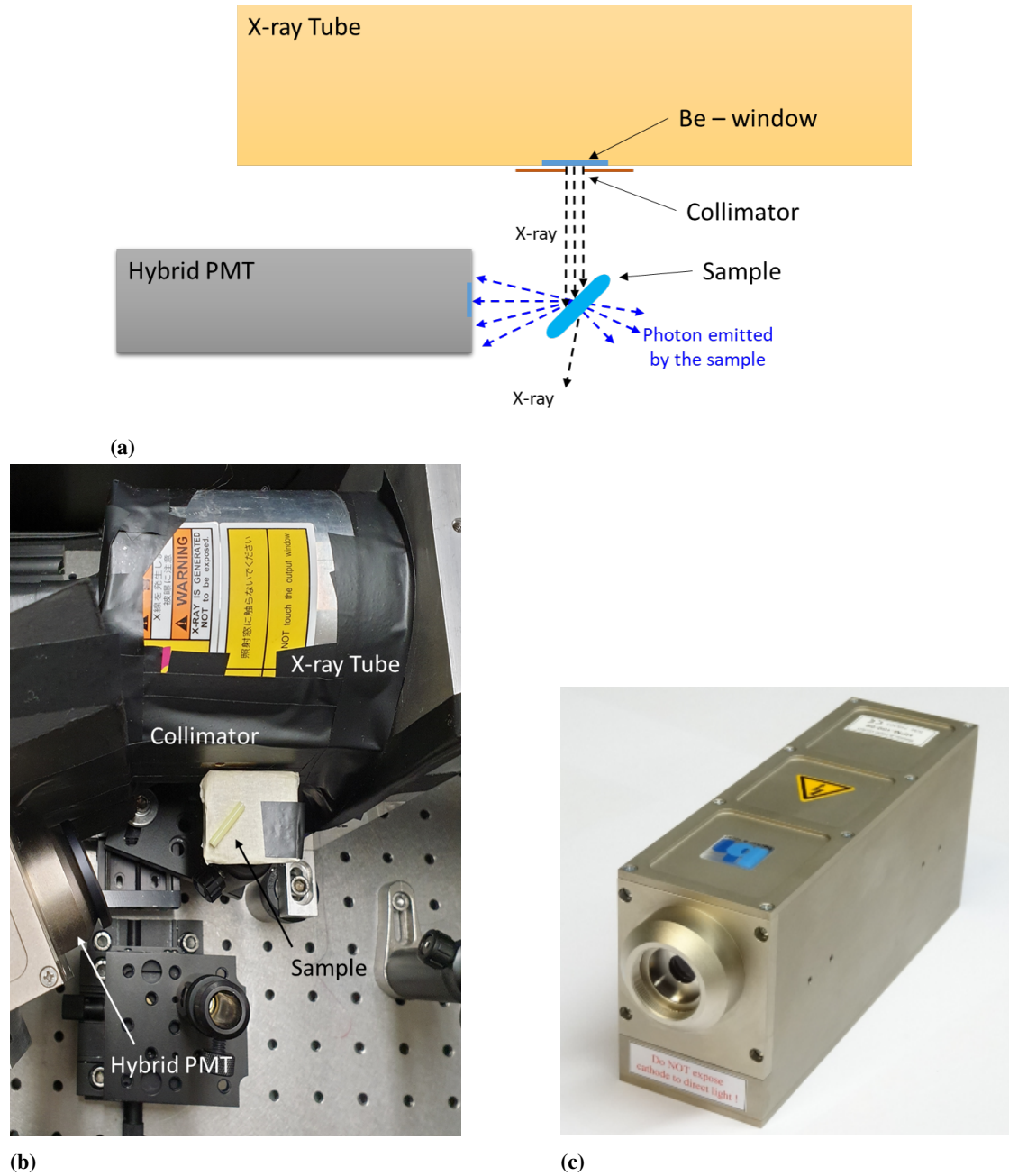


Figure 4.19 Scheme (a) and picture (b) of the experimental setup in the configuration used for the study of the scintillation dynamic of the nanocomposite. Picture of the relative Hybrid PMT Becker&Hickl HPM-100-07 (c).

scintillators [12]. Therefore with the effective decay time, a better understanding of the expected timing performance can be provided. The $(\tau_{d,eff})$ has been obtained using the harmonic average

	$\tau_{d;eff}$ (ns)	$\tau_{d;av}^{SC}$ (ns)	$\tau_{d;av}^{PL}$ (ns)
PMMA:0.1% MOF	1.0	7	5.5
PMMA:0.5% MOF	1.4	7	3.8
PMMA:2.5% MOF	1.2	10	2.9

Table 4.4 Effective and average decay time calculated through the fit results of the three rod-like nanocomposites with a concentration of MOFs equals to 0.1%, 0.5% and 2.5%. For a better comparison the photoluminescence average decay is reported.

Scintillation results	τ_r (ps)	τ_{d1} (ns)	τ_{d2} (ns)	τ_{d3} (ns)	ρ_{d1} (%)	ρ_{d2} (%)	ρ_{d3} (%)
PMMA:0.1% MOF	10±6	0.2	2.2	14	14	45	41
PMMA:0.5% MOF	25±12	0.1	2.6	13	7	52	41
PMMA:2.5% MOF	86±82	0.1	2.9	19	6	52	42

PL results	τ_1 (ns)	τ_2 (ns)	a_1 (%)	a_2 (%)	$\tau_{d;av}^{PL}$ (ns)
PMMA:0.1% MOF	5.5	–	100	–	5.5
PMMA:0.5% MOF	2.2	5.9	57	43	3.8
PMMA:2.5% MOF	2.4	4.4	78	22	2.9

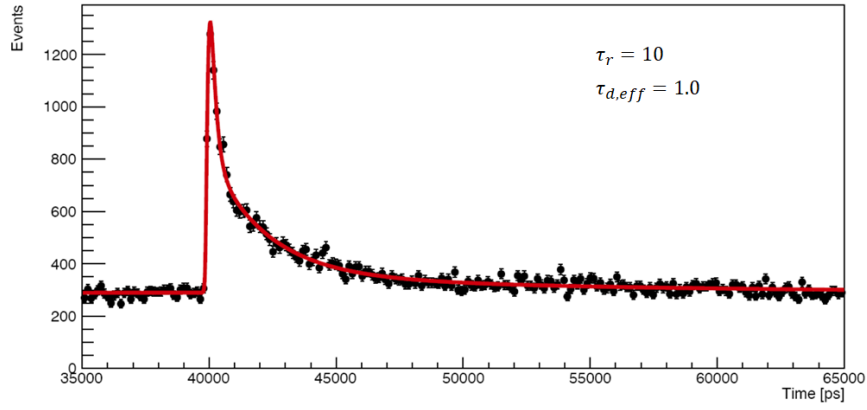
Table 4.5 (Top) Scintillation fit results of the three rod nanocomposites with concentration of MOFs equals to 0.1%, 0.5% and 2.5%. The error on the fit results has been estimated to be in the range of 15%. (Bottom) Photoluminescence results extracted from Tab.4.1.

in Eq. 1.11. The $\tau_{d;av}^{SC}$ allows to have a better comparison with the PL behavior and was calculated with the weighted average in Eq. 1.10. The results coming from these calculations are in Tab. 4.4 with $\tau_{d;av}^{PL}$ (see paragraph 4.1.3) for each tested sample. The scintillation pulses of the samples are reported in Fig. 4.20a, 4.20b and 4.20c, while the fit results are in Tab. 4.5.

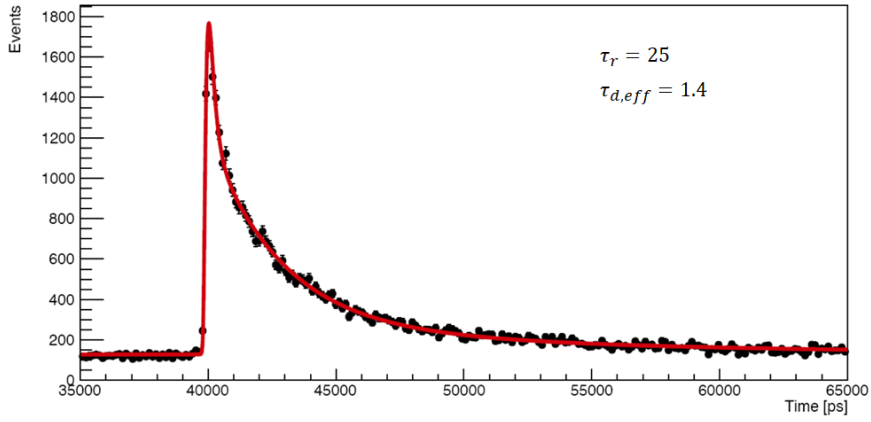
4.3.3 Discussion

The results show that the nanocomposites under study are very fast. In particular, their measured rise time was evaluated to be in the sub-100 ps range but it is affected by great uncertainty. This can be due to the performance limits of the used setup or by insufficient statistics to have a more precise fit response. Regarding the decay behavior, the PMMA:0.1% MOF has a fast first decay component whose weight is greater the one of the first components of the other two samples. Its second decay component, moreover, is faster than the other nanocomposites. All this reflects on a steeper decay behavior of the PMMA:0.1% MOF.

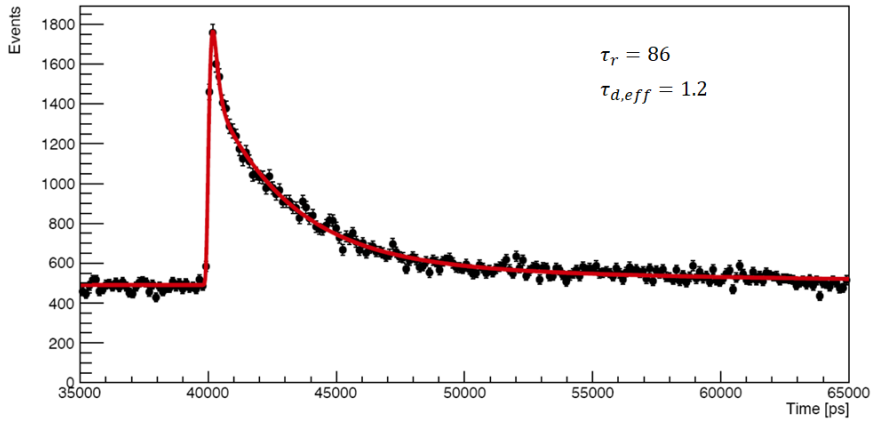
In any case, the difference in the effective decay times of the three nanocomposites is not enough to state with certainty which samples have the best timing properties. Indeed, $\tau_{d;eff}$



(a) Scintillation pulse about the rod of PMMA:0.1% MOF.



(b) Scintillation pulse about the rod of PMMA:0.5% MOF.



(c) Scintillation pulse about the rod of PMMA:2.5% MOF.

Figure 4.20 Scintillation pulses about the three rods with PMMA matrix. The results of the rise and decay time are showed.

resulted to be around 1 ns for all the tested samples. Then, in the first analysis, the different concentration does not affect $\tau_{d;eff}$ but during the experimental measurement, the number of the recorded event increased faster with higher concentrations. This is another proof that the radiation matter interaction was much strong when more MOFs are in the matrix. Looking at the rise time and ignoring its uncertainty for a moment, it seems that τ_r increases with increasing of the concentration.

The trends of the photoluminescence average decay time ($\tau_{d;av}^{PL}$) are not in agreement with respect to the scintillation one ($\tau_{d;av}^{SC}$). The reason could be due to the different mechanisms involved in the two processes. Especially, loss mechanisms could be distinct. Furthermore, a faster scintillation behavior should be reflected in better time resolution.

4.4 Coincidence time resolution

4.4.1 Materials and methods

The coincidence time resolution measurement has been performed for the nanocomposites at 0.5% of MOF in pixel geometries, both for PDMS matrix and PMMA ones. Moreover, the CTR of PMMA:2.5% MOF has been investigated.

The square pixel nanocomposites have been wrapped with a teflon reflector leaving the side of $2 \times 2 \text{ mm}^2$ uncovered since it is the one that has been coupled with the photodetector. On the other hand, the PMMA:2.5% MOF and PMMA:0.5% MOF, the two cylindrical pixels, have not been wrapped since there was the doubt that the reflector could have led to a dominant signal with respect to that of the sample.

Each nanocomposite has been put in coincidence to a reference crystal of LSO:Ce:0.2%Ca of size $2 \times 2 \times 3 \text{ mm}^3$ wrapped in teflon with 58 ps CTR. The samples and the reference were placed at the opposite sides of a ^{22}Na source. The samples were coupled to a Hamamatsu S13360-3050CS SiPM biased at 61 V and the leading edge threshold was set to 10 mV the leading edge threshold. Instead, the reference crystal was coupled to an FBK NUV-HD SiPMs biased at 39 V and here, the leading edge threshold was set to 20 mV yielding a CTR of 58 ± 3 ps FWHM. The signal coming from SiPMs was split, one part is read out by the high-frequency electronics for the time signal, the other part by an analog operational amplifier for the energy signal. Both the energy and the time signals are digitized by a LeCroy DDA735Zi oscilloscope with 3.5 GHz bandwidth and a sampling rate of 20 Gs/s for four channels [37]. The setup used for the measure is illustrated in Fig. 4.21.

The data acquired and used for the offline analysis, which was done with ROOT, were the following:

- integration of the energy signal of the reference crystal (charge);
- integration of the energy signal of the nanocomposite (charge);
- time difference between the time signals of nanocomposite and the reference crystal (time delay);
- time difference of the high-frequency signal (signal rise time).

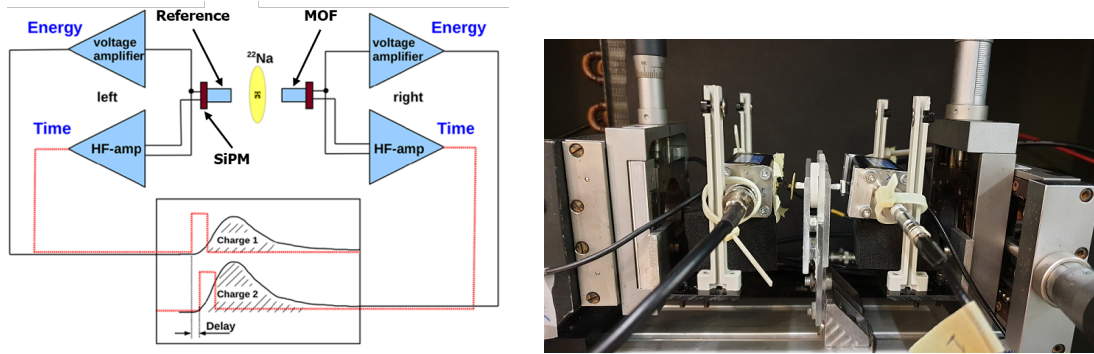


Figure 4.21 (Left) Illustration of the coincidence time resolution measurement setup (adapted from [37]) and a picture of it with both reference crystal and sample wrapped (right).

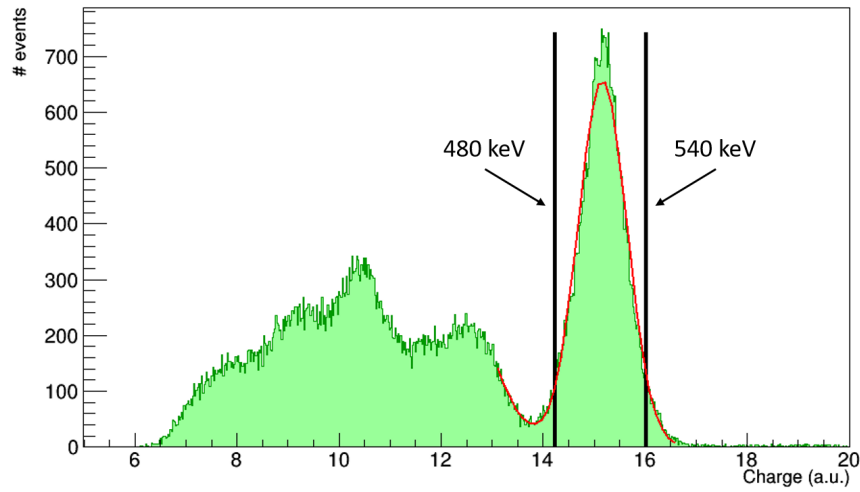


Figure 4.22 Charge histogram of the reference (LSO). In highlight the Gaussian function used for the fitting of the photopeak and the edges of the selection of the event at 511 keV.

More detailed description of the aforementioned setup can be found in [37].

A photopeak selection on the charge histograms of the reference (against each sample) was applied to only consider events that deposit 511 keV in LSO. The photopeak was fitted with a Gaussian function, whose center was made to correspond to 511 keV. Nevertheless, due to the system energy resolution, all the events between 480 keV and 540 keV can be considered those to 511 keV. Since the position of the reference crystal and the source was not changed, this spectrum was reasonably assumed to be identical for all the measurements, and so also the selection range. The charge histogram of the reference is illustrated in Fig. 4.22.

The selection, therefore, allows having the charge histograms of the nanocomposites based only on the events in coincidence with those at 511 keV in the LSO. From these histograms, different cutting edges have been chosen to build the time delay distribution for each sample.

The cutting edges might match the Compton edge which corresponds to the maximum amount of energy deposited by Compton interaction.

Then, the peak of the time delay distribution was fitted summing two Gaussian functions at free parameters and the CTR values at the FWHM of the fit function have been taken. This value contains that of the reference sample because of the configuration of the setup used. Therefore, to evaluate the CTR of the tested samples the time resolution of the reference crystal must be corrected according to Eq. 4.8.

$$CTR_{D1} = \sqrt{2 \cdot CTR_{measured}^2 - CTR_{LSO=58ps}^2} \quad (4.8)$$

The time pick off method employed for triggering the signals is subject to amplitude walk: given a fixed threshold, the signals with greater amplitude and faster rise-time cross the threshold before than the lower and slower signals. Therefore another correction, called *time walk correction*, can be applied to improve the CTR [38].

4.4.2 Results

Different cuts have been done to select the event on the charge histogram of the nanocomposites tested and find the best compromise between statistics and time resolution.

Square pixel of PDMS:0.5%MOF

The two time delay distributions of the square pixel of PDMS:0.5%MOF in Fig. 4.23b and Fig. 4.23c, have been created selecting those events beyond charge at 0.3 and 0.5 a.u. on charge histogram of the nanocomposite. As aforementioned, the CTR values coming from these two time delay distribution have been corrected for the time resolution of the reference and is resulted equal to 305 ps and 240 ps for the two selection positions, respectively. The time walk correction led to an improvement of the CTR value only for the less restrictive selection at 0.3 a.u. The improved CTR was 277 ps.

Square pixel of PMMA:0.5% MOF

With the same approach and selection positions (0.3 a.u. and 0.5 a.u.), the corrected CTR values of the square pixel of PMMA:0.5% MOF turned out to be 282 ps and 258 ps. In this case, the time walk correction did not lead to any improvement in the CTR values for both the event selections. The time delay distributions of this nanocomposite in square pixel geometry and its charge histogram are illustrated in Fig. 4.24.

Cylindrical pixel of PMMA:0.5% MOF

Moreover, the cylindrical pixel unwrapped of PMMA:0.5% MOF has been studied. Its charge histogram is found in Fig. 4.25a and three event selections have been made on it: one more large at 0.3 a.u., one at 0.5 a.u. and another more restrictive at 0.8 a.u. The first led to a time delay distribution with a shape with two peaks (see Fig. 4.25b). The CTR was extrapolated from the right peak and corrected for the reference time resolution. Then, the CTR value resulted to be

211 ps. Time walk correction could not be applied. The selection at 0.5 a.u. lead to a time delay distribution with the same two peaks but no stable fit has been obtained. While for the latter energy cut the number of remaining events was too little to provide a meaningful time delay distribution.

Cylindrical pixel of PMMA:2.5% MOF

For the unwrapped cylindrical pixel of PMMA:2.5% MOF, the selection positions on its charge histogram (Fig. 4.26) have been chosen beyond charge at 0.3, 0.5, and 0.8 a.u. For this sample, the time walk correction led to a significant improvement for all the event selections. Indeed, the CTR values improved from 326 ps to 242 ps for the selection on charge histogram beyond 0.3 a.u., from 304 ps to 229 ps selecting beyond 0.5 a.u., and from 281 ps to 233 ps selecting beyond 0.8. a.u. The time delay distributions of this nanocomposite are in Fig. 4.27.

For this nanocomposite, it was possible to estimate the theoretical CTR value, or in other words, its intrinsic lower limit, of the material through the Eq. 4.9 deriving from an analytic model studied by S. Vinogradov [39] and adapted by S. Gundacker [12]:

$$CTR_{intr. l. l.} = 3.33 \sqrt{\tau_{d;eff} \frac{1.57 \cdot \tau_r + 1.13 \cdot \sigma_{SPTR+PTS}}{LY@Energy}} \quad (4.9)$$

where the term $\sigma_{SPTR+PTS}$ denotes the convolution of the single-photon time resolution (SPTR) of the SiPM used in the experimental analysis of the CTR with the photon transfer time spread (PTS) of the sample. As mentioned in the work by S. Gundacker, the $\sigma_{SPTR+PTS}$ is described by a Gaussian whose sigma has been calculated to be ~ 69 ps [12].

Then considering $ILY_{PMMA:2.5\% MOF} = 1.7$ ph/keV, the maximum amount of deposited energy equals to 340 keV due to the Compton effect at 511 keV, $LTE_{MOF} = 0.74$, the weighted $PDE_{MOF} = 0.49$, $\tau_r = 86$ ps and $\tau_{d;eff} = 1.2$ ns, the $CTR_{intr. l. l.}$ resulted to be as low as ~ 118 ps.

SiPM detector and Meltmount response

To understand the impact on the statistic of the SiPM and the Meltmount utilised, their statistic have been investigated. In particular, two event selections on their charge histogram (see Fig. 4.28) have been studied. Selecting beyond 0.1 a.u. there was a discrete number of events (585) but selecting beyond 0.3 a.u. only a negligible number of events remained (49).

In Tab. 4.6 are summarized, for each sample, the cut position, the number of events coming from it, and the values of the CTR extrapolated with and without the time walk correction. The CTR and CTR_{twc} errors have been estimated to be in the range of 6%.

4.4.3 Discussion

All the charge histograms do not show any photopeak with respect to the reference crystal because, as aforementioned in paragraph 4.2.3, the effective mass of the nanocomposite is not high enough to allow a photoelectric interaction with the ionizing radiation. Different event selections show that with more aggressive ones there is a significant improvement in CTR but the

	Cut position (a.u)	# event	CTR (ps)	CTR _{twc} (ps)
PDMS:0.5% sp	0.3	~10000	305	277
	0.5	~3000	240	–
PMMA:0.5% sp	0.3	~4500	282	–
	0.5	~1900	258	–
PMMA:0.5% sp	0.3	~3000	211	–
	0.5	~800	–	–
PMMA:2.5% cp	0.3	~19600	326	242
	0.5	~8200	304	229
	0.8	~1900	280	233

Table 4.6 Data about CTR analysis of the tested nanocomposites where *sp* and *cp* correspond to square and cylindrical pixel, respectively. The reported CTR values are corrected for the reference time resolution. The CTR and CTR_{twc} errors have been estimated to be in the range of 6%.

statistic is not always sufficient to get further improvement with the time walk correction. For instance, for the PMMA:2.5% MOF, the time walk correction applied to the aggressive selection at 0.8 a.u. leads to a worse improvement with respect to the selection at 0.5 a.u.

Further investigations should be done to understand the ambiguous behavior of the CTR values between the two square pixels of PDMS:0.5% MOF and PMMA:0.5% MOF. The latter has a better CTR if the event selection is done at 0.3 a.u. but not if it is done at 0.5 a.u. Therefore, no statement can be given about which of the two samples has the best time resolution.

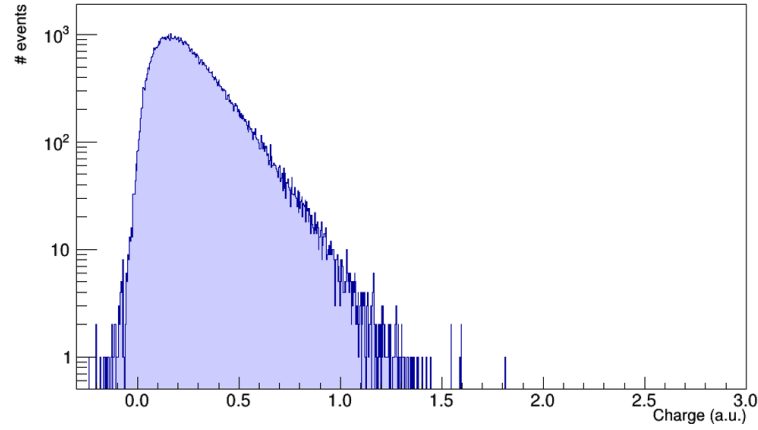
Since each nanocomposite has events that generate the maximum amount of charge around 1.5 a.u. which is much lower than that of a generic crystal, such as the BGO (35 a.u., inset of Fig. 4.18), then the SiPM and the Meltmount could give a signal comparable with that of the nanocomposite. Therefore, to understand the impact on the statistic of the SiPM and of the Meltmount utilised, their statistics have been investigated. The two event selections on the charge histogram highlight that if the event selection about nanocomposites involved events beyond 0.3 a.u. a negligible number of events deriving from SiPM and Meltmount affects the time delay distribution of the nanocomposite.

However, in the time delay distribution of PMMA:0.5% MOF with the cylindrical shape, a pronounced peak appears in the left region (Fig.4.25b). This peak is also observed in the range of -200 ps of the other time delay distributions but in a much less evident way. It is most likely coming from gamma interactions with the SiPM or its protection window and causes a large blur in time delay distribution deteriorating the time resolution.

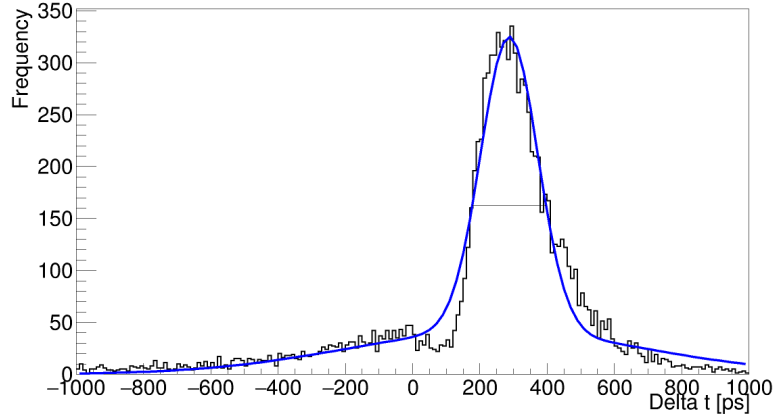
With an accurate selection, only the right peak can be selected and the CTR can be extracted. Nevertheless, the limited statistic makes inaccurate the process.

Overall, the better timing performance of this lower concentrated cylindrical pixel compared to that of the PMMA:2.5% MOF is in agreement with the average behavior of the scintillation pulse. The nanocomposite with a minor rise and average decay time has a lower CTR.

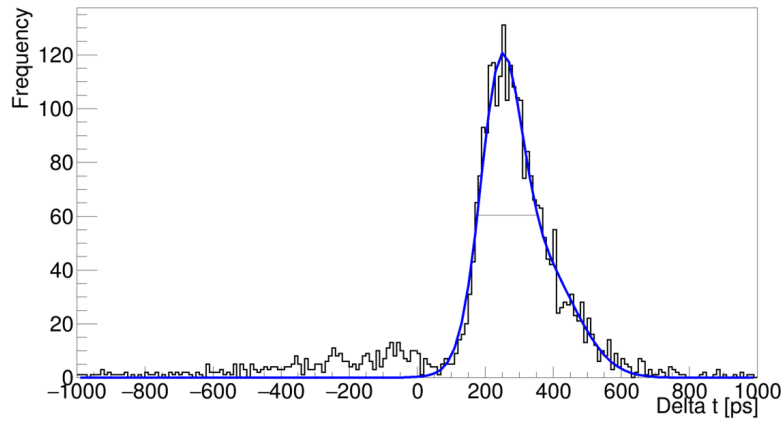
The CTR = 229 ps of the PMMA:2.5% MOF resulted to be 1.9 times higher than its intrinsic lower limit. This difference could be due to the internal scattering and self-absorption since they deteriorate the light transport blurring the delay distribution because some photons can be extracted with different delays. Moreover, these effects can be more consistent at higher concentrations.



(a) Charge histogram of the square pixel of PMMA:0.5% MOF.

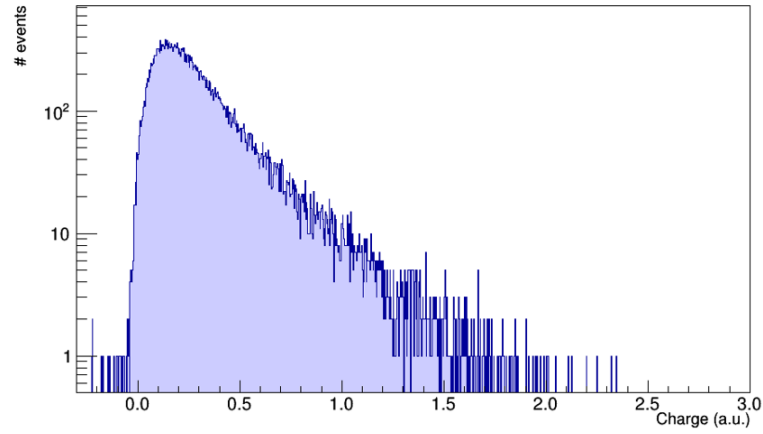


(b) Time delay distribution histogram based on event selection beyond 0.3 a.u. about (a).

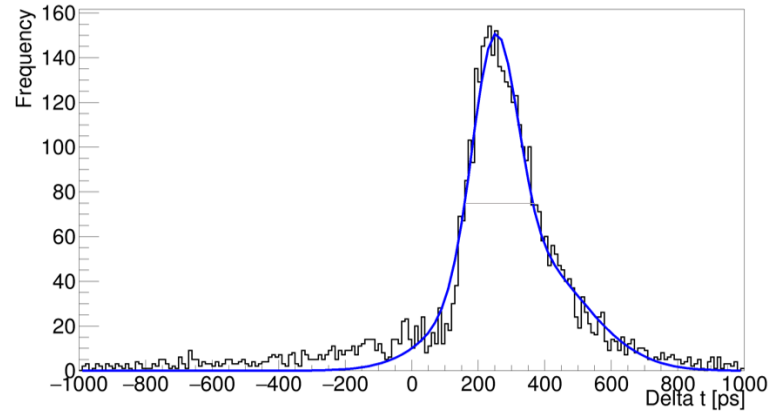


(c) Time delay distribution histogram based on event selection beyond 0.5 a.u. about (a).

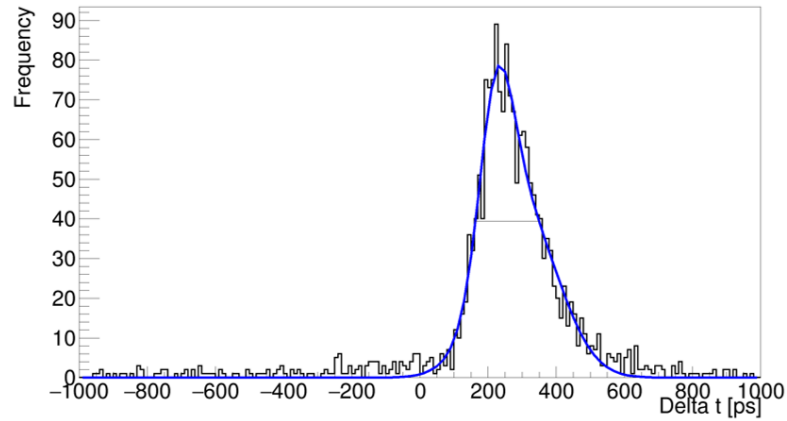
Figure 4.23 Charge and time delay distributions based on two event selections about charge histogram of the square pixel of PDMS:0.5% MOF.



(a) Charge histogram the square pixel PMMA:0.5% MOF.

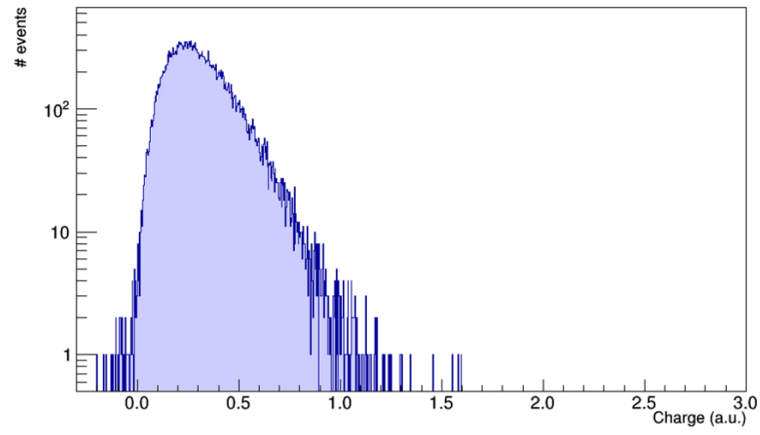


(b) Time delay distribution histogram based on the selection of event beyond charge at 0.3 a.u. about (a).

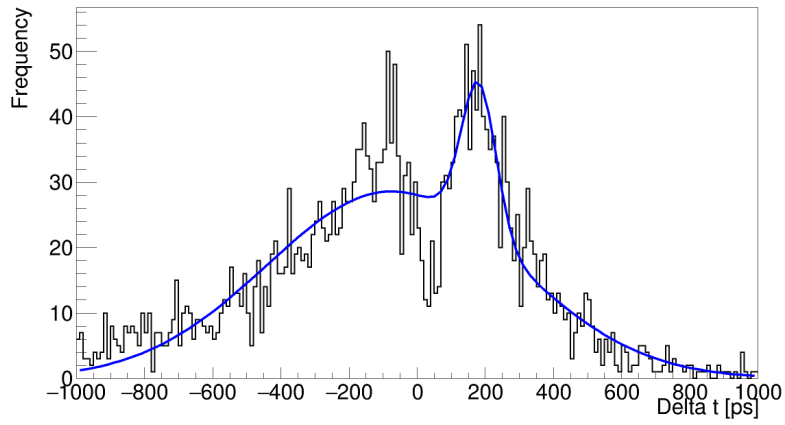


(c) Time delay distribution histogram based on the selection of event beyond charge at 0.5 a.u. about (a).

Figure 4.24 Charge and time delay distributions based on two event selection about charge histogram of the square pixel of PMMA:0.5% MOF.



(a) Charge histogram of the cylindrical pixel of PMMA:0.5% MOF.



(b) Time delay distribution histogram based on event selection of events beyond charge at 0.3 a.u. about (a).

Figure 4.25 Charge and time delay distributions based on the selection of events about charge histogram of the cylindrical pixel of PMMA:0.5% MOF.

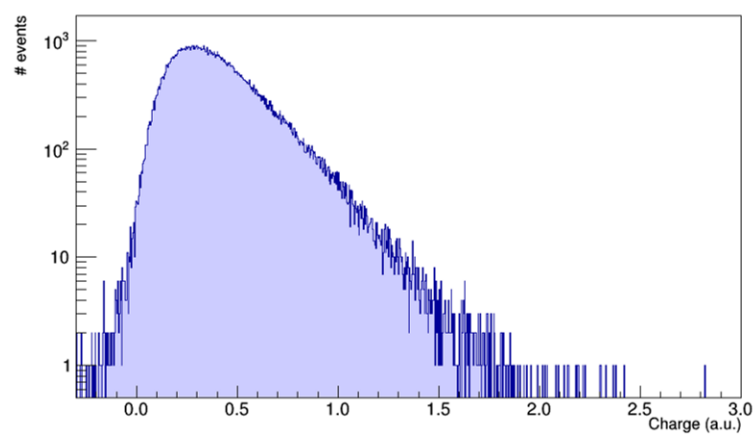
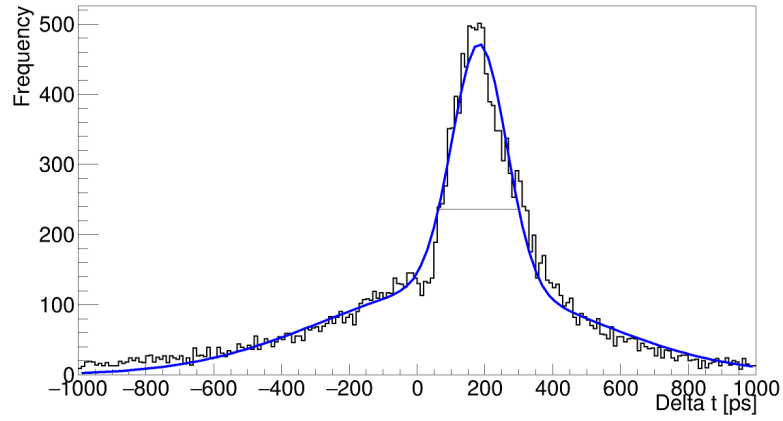
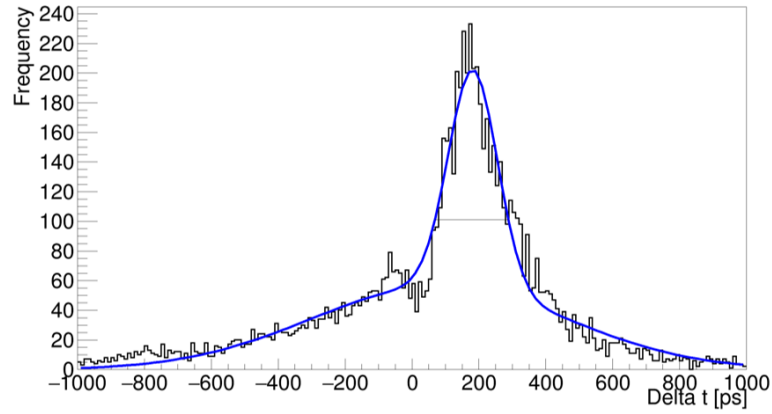


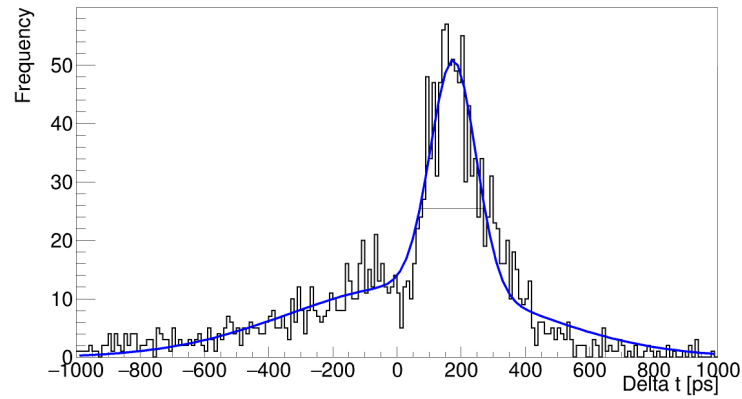
Figure 4.26 Charge histogram of the cylindrical pixel of PMMA:2.5% MOF.



(a) Time delay distribution histogram based on the selection of events beyond charge at 0.3 a.u. about charge histogram in Fig. 4.26).



(b) Time delay distribution histogram based on the selection of events beyond charge at 0.5 a.u. about charge histogram in Fig. 4.26).



(c) Time delay distribution histogram based on the selection of events beyond charge at 0.8 a.u. about charge histogram in Fig. 4.26).

Figure 4.27 Time delay distributions based on three distinct selections of events about cylindrical pixel PMMA:2.5% MOF.

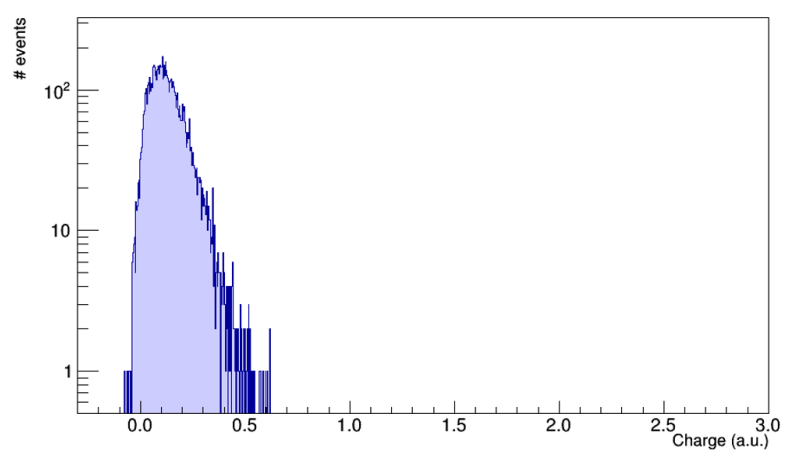


Figure 4.28 Charge histogram of SiPM detector and Meltmount.

Chapter 5

Conclusions and Outlook

In this Master thesis project metal-organic framework-based composites designed for TOF-PET imaging have been investigated.

The synthesis and the optical investigation have been performed at the Materials Science Department (UNIMIB). The accurate study of their scintillation properties related to the TOF-PET imaging has been carried out with forefront experimental techniques in the CERN Crystal Clear laboratory in Geneva, Switzerland.

The first part of this work concerned the study of the PL properties to verify that the emission properties are maintained in the composite and the results showed that increasing the concentration in PMMA nanocomposites, radiativeless mechanisms increase shortening the emission decay which is detrimental for the quantum yield. However, to have good scintillators and have an efficient scintillation response, nanocomposites with high concentrations are needed. Indeed, after this preliminary study, investigating the scintillation properties, the higher concentrated nanocomposite resulted to have the best rate of events and LY.

From the studies of the scintillation pulse, it emerged that the examined nanocomposites are very fast. The measured rise times are in the sub-100 ps range, which is close to the limit of the time resolution of the instrumental setup.

Therefore, MOFs composite could potentially offer the desired level of structural control and could be a viable alternative as radiation detectors for TOF-PET imaging due to their fast scintillation since the prototype scintillators already show the state-of-the-art CTR values for commercial devices.

Further improvements must be addressed: in particular, considering the fast response of the composite scintillators, efforts must be devoted to enhancing the LY, by increasing the efficiency of ionizing radiation absorption and reducing light losses due to the internal scattering and self-absorption, such as using others organic ligands or dopants to increase the Stokes shift, or use an optically active polymer able to sensitize the emitter ligand. Moreover, next developments could regard the implementation of MOFs-based composites in heterostructure scintillators, composed of alternating plates of MOFs-based composites and high-density crystals able to efficiently absorb the ionizing radiation. Therefore, the number of events detected in the overall system would increase leading to a prospective increase of LY and consequently even to a better CTR.

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