

From sintering to particle discrimination: New opportunities in Metal-Organic Frameworks scintillators

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1 From sintering to particle discrimination: New opportunities in Metal-Organic 2 Frameworks scintillators 3 4 Vincent Villemot, Nicolas Dufour, Sharvanee Mauree, Benoît Sabot, Guillaume H. V. Bertrand, 5 Matthieu Hamel 6 7 8 V. Villemot*, N. Dufour, S. Mauree, Dr. B. Sabot, Dr. G. H. V. Bertrand, Dr. M. Hamel* 9 Université Paris Saclay, CEA, List, F-91120 Palaiseau, France. 10 vincent.villemot@cea.fr and matthieu.hamel@cea.fr Orcid numbers: 0000-0002-9478-6651 (VV), 0000-0001-8551-709X (ND), 0000-0003-3043-11 12 8006 (BS), 0000-0003-2061-9241 (GHVB), 0000-0002-3499-3966 (MH). 13 14 Keywords: MOF, scintillator, densification, photoluminescence, radioluminescence, MCNP, 15 discrimination 16 17 Abstract: 18 The characterization of a scintillating Metal Organic Framework (MOF) is not straightforward, 19 mainly due to the small size and low density of the material. In this context, we present herein 20 a generic method to give an easy access to the determination of a key parameter in the 21 scintillation field, namely the light output. To reach this, MOF-205 was first synthesized as 22 millimetric-size single crystals then sintered under pressure and temperature conditions to afford a pellet. The density was increased by 300% while maintaining optical properties on par 23 24 with scintillation application. The as-prepared scintillator was then characterized in terms of photoluminescence (UV-excited emission spectrum, time-correlated single photon counting) 25 and radioluminescence spectroscopy (beta-excited emission spectrum, alpha, beta and gamma 26 27 pulse height spectra, alpha/beta and alpha/gamma discrimination). Results were compared with commercial BC-404 plastic scintillator performances as well as supported by MCNP6.2 28 29 simulation. 30 1. Introduction 31 32 Methods to detect, qualify and quantify ionizing radiations were introduced soon after the 33 discovery of radioactivity by Henri Becquerel in 1896. Currently, numerous applications benefit 34 from this field, ranging from nuclear activities, research in high-energy physics, astronomy,

homeland security and medicine. Depending on the radionuclide to be detected, various
disintegrations can occur, the most common and probable leading to the emission of alpha or
beta particles often followed by de-emissions producing X and/or gamma rays. These ionizing
radiations can be detected with scintillators, which are materials that are efficient to produce
light when exposed to such radiations. This specific class of photoluminescent materials is
divided into two main categories, namely inorganic and organic scintillators. ^[1] The former
subclass appeared as early as 1895 (barium tetracyanoplatinate(II) BaPt(CN)4) ^[2]). The later was
pioneered when the use of naphthalene was first reported in 1947.[3] Since these seminal
publications, many efforts have been performed in the two chemistry worlds for the quest of
the 'best' scintillator. However, both have pros and cons and currently no photoluminescent
material represents the Holy Grail that could fulfil all requirement in terms of radiation
detection (among others: detection efficiency against production cost). In this context, scientists
have considered using advantages from both worlds, hence leading to a various range of
scintillators such as sol-gel, hybrid materials or nanoparticles-loaded plastics. ^[4] Most
particularly, composite scintillators stand out as they can bypass a lot of limitations. The core
idea is to take a known efficient scintillator, mainly an organic or inorganic single crystal, and
embed them into a matrix of suitable polymer. This will give access to what can be described
as a polycrystalline scintillator. As single crystals are often hard to produce in large scale or are
not very stable towards ambient condition (mechanical weakness, humidity and temperature
dependency), this technology affords a way to combine large quantity of efficient scintillator
and stability-aimed encapsulation.
Metal organic frameworks (MOFs) are a class of hybrid materials. ^[5] Under their crystalline
form, they have found great interest to many researchers in a wide variety of fields because of
their great versatility. ^[6] They are constructed of inorganic nodes linked with each other by
organic ligands. Therefore, the modification of one or both bricks allows modifying the final
properties the only limitation being thus the creativity of the scientist. Allendorf et al. were the

61	first to highlight the possibility to use MOFs as potent scintillators. They observed decent light
62	outputs (up to 22% of anthracene, ca. 3,300 ph·MeV ⁻¹) by switching traditional organic linkers
63	for a dicarboxylated trans-stilbene, an already known and efficient scintillating molecule. ^[7]
64	Thanks to the above mentioned high degree of versatility of MOF construction, some
65	researchers, again using ligands based on scintillating molecules, have also assembled
66	frameworks based on traditional inorganic bricks and heavier metals to increase the stopping
67	power of X-rays. For example, Wang et al. have synthesized two different 9,10-di(para-
68	carboxyphenyl)anthracene (DPA)-based MOFs,[8] where one was connected to Zr nodes
69	whereas the other to Hf nodes. As the two materials have different X-ray cross sections, it was
70	possible to show a qualitative increased sensitivity for Hf-MOF.
71	Recently, new contributions have emerged involving Metal-Organic Frameworks as
72	scintillators, having in mind their use in medical applications such as TOF-PET detectors. [9]
73	Perego et al. have embedded the DPA-based Zr-MOF (previously synthesized by Wang ^[8])
74	inside two polymeric matrices: poly(dimethylsiloxane) (PDMS) and poly(methyl methacrylate)
75	(PMMA). As MOFs can be hard to synthesize in large crystals, difficult to scale up and tricky
76	to handle, composite materials seem to be the go-to solution to test them as scintillators.
77	However, several limitations are foreseen with the incorporation of a MOF inside a matrix, and
78	in general to the characterization of MOFs as scintillators. Despite efforts by chemists to
79	synthesize MOF nanocrystals, these are subject to strong light scattering already at a low
80	percentage of incorporation in the polymer matrix, which can lead to turbidity observed at
81	loading as low as 0.5 weight%. This is mainly cause by the incorrect matching between the
82	matrix and MOFs refractive index which lead to light scattering. This effect coupled to the
83	numerous interfaces between the matrix and the embedded MOF can thus lead to strong
84	deviation from the optimal light collection. These cumulated factors are altering the global
85	optical properties and leading to a moderate scintillating material (6% the light output of
86	anthracene, which is ca. 1,000 ph·MeV ⁻¹). Other literature from this field generally describes

analytical methods that have to be adapted to small-size and low-density MOF materials, for
example with Ion Beam Induced Luminescence ^[7] (IBIL) or small X-ray tubes, ^[8] . This
experiments require high dose delivery ^[8, 9] or tedious characterization in liquid suspension. ^[8]
Such techniques are useful but developing a universal characterization method for scintillating
MOFs the closest to their final use, which means confronted to the presence of radionuclides
and without form factor (e.g. single crystals dispersed in a liquid) would be of great value for
the scientific community, and that was the core idea at the root of this study.
To overcome these issues, this work presents two major contributions leading to scintillating
materials made from MOFs. The first concerns the densification by sintering until translucent
media are reached. ^[10] The second concerns the nearly transparent pellet entirely composed by
a luminescent MOF, and its use as scintillator. This application becomes particularly natural
and of practical use to determine one of the scintillator key parameter: the light output.
Experimental results, validated by particle radiation transport simulations performed with the
MCNP6.2 Monte Carlo code allowed for the first time to characterize a Metal Organic
Framework under alpha, beta and gamma excitation, and to observe a light output that can
compete with a commercial plastic scintillator (BC-404, Saint-Gobain Crystals and
$Detectors^{[]}$. Furthermore the hybrid nature of our sintered MOF was put in the perspective
of classical inorganic and organic crystal scintillation. Those fields are known to demonstrate
good particle discrimination by PSD. This approach was applied to our materials and
unprecedented particle discrimination with scintillating MOFs has been reached, confirming
precedent hint from Allendorf et al.[15]

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2. Results and discussion

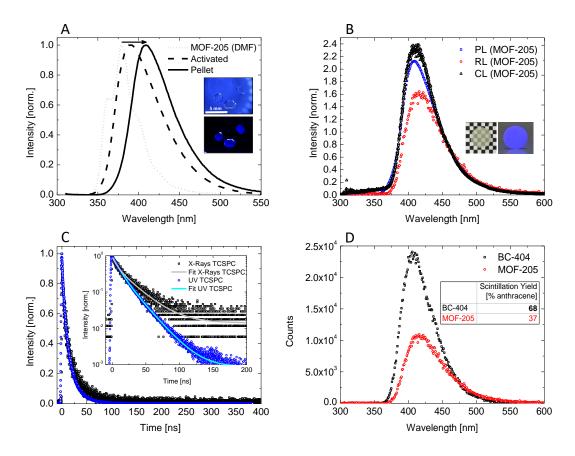


Figure 1. Structural and photophysical properties of sintered MOF-205. A) Photoluminescence spectra of MOF-205 in DMF (dotted line), activated (dashed line) and pellet (solid line). Inset are pictures of millimetric single crystals under visible light and under 365 nm excitation light. B) Normalized steady-state Photoluminescence (PL), Radioluminescence (RL) and Cathodoluminescence (CL) spectra of sintered MOF-205. Inset are pictures of pellet under visible light and under 365 nm excitation light (excitation source was placed behind the pellet). C) Time-Correlated Single Photon Counting (TCSPC) of sintered MOF-205 after 274 nm excitation (blue) and X-rays excitation (black). Decay values are the result of a biexponential fitting with a $R^2 = 0.99$. D) Radioluminescence spectra of BC-404 and MOF-205 (both are \varnothing 13 mm and thickness 400 μ m). Area integration allows to recover the scintillation efficiency values.

As demonstrated in many contributions, MOF synthesis is tricky and requires attention as an impurity can have a large impact on the final photophysical properties.^[13] As a case study, we chose a MOF where the secondary building unit is Zn₄O, linked with two different organic linkers: 1,3,5-tris(4-carboxyphenyl)benzene (H₃BTB) and 2,6-naphthalene dicarboxylate (2,6-NDC), which is also named MOF-205 or DUT-6.^[14,15] It was selected as a potent candidate thanks to its photoluminescent properties that comply with standard plastic scintillators: fast decay time and emission wavelength centered around 420 nm. These interesting features are

carry by the naphthalene moiety, which is a well-known molecule in the scintillation field. ^[16]
The second reason is that this framework presents a cubic lattice structure, which is compliant
with sintering application, a key in densification. Theoretically, under uniaxial pressure planes
of cubic structures should move isotropically and finally result in a material densification, a
result that would be less easy to achieve with non-cubic lattices ^[10] , or anisotropic collapses.
Here we propose a densification of MOF under two external stimuli: pressure and temperature.
This has already been demonstrated by Zacharia et al. only under the action of pressure for
MOF-177, a MOF that is similar to MOF-205. ^[17] This trend remains marginal as the purpose
of synthesizing MOF is, classically, to use their porosity properties, which is not compatible
with densification.
Thus, MOF-205 was synthesized to obtain large, pure, millimeter-sized crystals (Inset of Figure
1.A), was sintered and fully characterized (see Supporting Information, Figure S1). As heat can
promote the plastic displacement leading to densification, temperature limits should be defined
in order to prevent any parasitic degradation of the (photo)physical properties. Thus, thermal
decomposition behavior was investigated in order to characterize its thermal stability. As shown
in Figure S2, thermogravimetric analysis (TGA) shows two characteristic weight losses. The
first continuous weight loss of 9.9% in the temperature range from 30 $^{\circ}\text{C}$ to 350 $^{\circ}\text{C}$ corresponds
to the desorption of guest molecules. The second drastic loss of 66.4% occurring at 450 $^{\circ}\text{C}$
corresponds to the decomposition of the frameworks to ZnO and organic byproduct. From this
analysis, we decided to constrain the sintering to an operating window between 30 °C and
200 °C in order to avoid any deterioration of the MOF during this process. Thus, activated
powder of MOF-205 was pressed under 15 tons in a 13 mm diameter dye at 100 °C for 20 min,
corresponding to a pressure of 1.1 GPa. The resulting pellet (Inset of Figure 1.B) presented a
thickness of $400\pm20~\mu m$ and a mass of 82 mg. Considering the pellet as a perfect cylinder, a
density of 1.56 ± 0.08 was calculated, which represents a remarkable increase of 300%
compared to its original density (0.38). ^[14] Furthermore, the resulting pellet displayed promising

163	photophysical properties. Main spectral characteristics were obtained from either UV
164	photluminescence (PL) or ionizing radiation such as radioluminescence (RL) with an $^{90}\mathrm{Sr}/^{90}\mathrm{Y}$
165	beta source or cathodoluminescence (CL) with an X-ray excitation. The results are shown in
166	Figure 1.A-D, and discuss below.
167	At the origin of our composite scintillator, MOF-205 in DMF presents an emission of 380 nm
168	with characteristic vibronic structure of linker in its dilute form (Figure 1.A). This is
169	characteristic of a ligand-centered emission. As already mentioned in many publications,
170	frameworks are likely to be dependent on their environment, guest molecules or impurities
171	trapped inside their porosity. Fluorescence is especially sensitive to external stimuli when it
172	arises from the linker only as is the case for MOF-5 for example. ^[18] Hence, upon activation the
173	material looses its fine structure and shows a Gaussian-type emission centered at higher
174	wavelengths (394 nm). Then after pressing, the pellet shows a slightly different steady-state
175	photoluminescence as the fluorescence maximum undergoes a shift to 409 nm (Figure 1.B).
176	This wavelength increase could be explained by larger π overlaps between the ligands due to
177	the densification of the material and the reduction of the ligands distance to each other. Thus,
178	the energy gap would be reduced and would result in a bathochromic shift at the image of the
179	ligand in its solid form ($\lambda_{em} = 452 \text{ nm}$) (Figure S3). This assumption is confirmed by a
180	comparison of the time-resolved fluorescence spectra. Under the effect of pressure and
181	temperature the material therefore tends to amorphise and favours a spatial rearrangement of
182	the ligands which leads to emission at a higher wavelength. This is confirmed as the pellet
183	shows no X-ray diffraction. This trend is as also demonstrated by Zacharia et al. for a similar
184	MOF. ^[17] However, we assume that this structural change remains minor as the average lifetime
185	is only slightly changed compared to pure activated MOF-205 single crystal (Figure S4). This
186	results collectively show that MOF-205 as a single crystal or sintered as a pellet have the same
187	photophysical behavior. Sintered pellets are hence a good sudo-sample to judge the scintillation

188	response of a MOF. Pellets are also more practical to use andstarting from this point, we are
189	considering the pellets as scintillating material in their own rights.
190	Radioluminescence (RL) and cathodoluminescence (CL), contrary to PL, allow the
191	investigation of excited states by ionization with radionuclides. As known, ionization process
192	is quite different from PL as ionization can lead to several changes in the electronic and
193	molecular structure of matter, thus expectable discrepancies in emission wavelength or/and in
194	lifetime. Figure 1.B compares normalized PL, RL and CL state spectra. Since RL and CL/PL
195	are recorded in transmission and front face, respectively, it is possible to notice several changes
196	in the shape of the Gaussian-type emission. This is mainly due to reabsorption and diffusion
197	occurring within the pellet. However, since traditional scintillation measurements are usually
198	performed in transmission, the RL experiment is closer to the application measurement method.
199	Figure 1.C represents the Time-Correlated Single Photon Counting (TCSPC) of sintered MOF-
200	205 after 274 nm excitation (blue) and X-rays excitation (black). It is interesting to note that
201	under X-rays excitation the pellet shows a fast and slow component in similar magnitudes as
202	under UV excitation. However, the weights of each components are different. Thus, the average
203	lifetime increases from 14.8 to 17.8 ns (Figure S5). This could be explained by a larger
204	population.
205	To highlight the use of sintered pellet of MOF-205, RL measurements were carried out with a
206	well-known reference in the scintillation field, namely BC-404 (Saint-Gobain Crystals and
207	Detectors) with same size and shape: a cylinder with 13 mm diameter and 400 μm thickness.
208	Both materials can thus be compared, provided that the experimental set up is identical as well.
209	This is shown in a radioluminescence experiments presented in Figure 1.D. As the area under
210	the curve corresponds to the amount of emitted photons, it is possible to estimate a scintillation
211	efficiency by a rule of thumb. MOF-205 emits 55% of what the BC-404 is capable. In other
212	words, this means that MOF-205 has a light output of 37% compared to anthracene, as the BC-

213	404 is 68% according to its datasheet. Considering that anthracene is $\approx 15,000 \text{ ph} \cdot \text{MeV}^{-1}$,
214	the light output of the sintered MOF-205 is thus around 5,500 ph·MeV ⁻¹ . The above results
215	validate the concept of a sintered MOF-205 as an intrinsic scintillator and places it above other
216	MOF-based scintillators as far as light output is concerned.
217	As the pellets are quite thin, the use of alpha-emitting source is obvious in terms of
218	characterization with radionuclides. Alpha emitters have a short penetration distance in matter,
219	and therefore ionize the pellet by depositing all their energy as shown by simulation (Inset of
220	Figure 2.A). For instance, the alpha emitter ²⁴⁴ Cm presents two characteristics energy lines at
221	$5.804~\mathrm{MeV}$ (76.7%) and $5.762~\mathrm{MeV}$ (23.3%). [19] With this energy, alpha particles from $^{244}\mathrm{Cm}$
222	are fully stopped within 400 μm of both scintillators, as it was confirmed by MCNP6.2
223	simulation. The maximum interaction depth was simulated at 37 μm and 45 μm for MOF-205
224	and BC-404, respectively. We explain this interaction depth difference from the MOF-205
225	higher density. Due to the detector's resolution and small energy difference between the two
226	alpha rays, it is expected that a single Gaussian-like spectra would be observed. In addition,
227	considering large ionization quenching that are classically encountered with alpha emitters in
228	plastic scintillators (12% of total energy), we expect to see the full absorption peak of the ²⁴⁴ Cm
229	alphas around 560 keV. ^[20] Results in Figure 2.A show that both BC-404 and MOF-205 present
230	a full absorption of ²⁴⁴ Cm at channels 18500 and 6500, respectively. However, the light output
231	of the latter was quantified and estimated at 57% the one of BC-404, hence the Gaussian mean
232	value should be expected at higher channel value (\approx 10,000). One hypothesis is the loss of
233	photons due to scattering in the MOFs, which is not as transparent as BC-404 plastic scintillator.
234	This was verified by measuring a pellet twice the width. The blue curve of an $800~\mu m$ thin
235	MOF-205 in Figure 2.A shows that the Gaussian peak is very close to the photomultiplier tube
236	noise, thus highlighting the importance of transparency. This is combined with the higher
237	stopping power of MOF-205 as was mentioned before, thus leading to an even more localized
238	interaction (ionization quenching), magnifying the light loss by self-quenching and increasing

the pathway for photon transport within this material. To confirm this hypothesis, beta acquisitions were carried out.

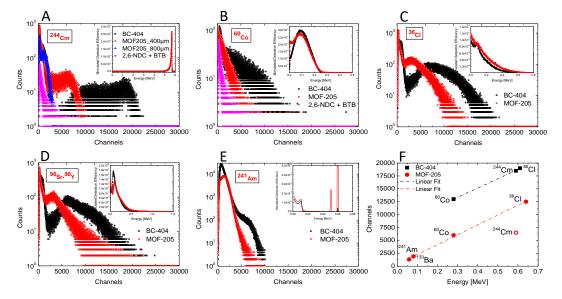


Figure 2. Comparison between scintillation performances of MOF-205 and BC-404.

Histogram of scintillation data for BC-404 (black), MOF-205_400μm (red), MOF-205_800 μm (blue) and 2,6-NDC/BTB in stoichiometric quantity (pink) in presence of A) ²⁴⁴Cm, B) ⁶⁰Co, C) ³⁶Cl and D) ⁹⁰Sr-⁹⁰Y. E) ²⁴¹Am pulse coincidence spectra. Inset in each graph represents the simulated pulse height spectrum. F) Channel position of the scintillators' response versus

impinging energy.

Beta emission spectra are continuous and beta particles present deeper tracks in the matter than alpha particles, resulting in full or partial energy deposition in the detector, depending of the incident energy. Three beta radionuclides were used in this study with their main emission as follows: 60 Co ($E_{\beta}^{mean} = 95 \text{ keV}$, $E_{\beta}^{max} = 317 \text{ keV}$), 36 Cl ($E_{\beta}^{mean} = 316 \text{ keV}$, $E_{\beta}^{max} = 709 \text{ keV}$) and 90 Sr/ 90 Y ($E_{\beta}^{mean} = 196 \text{ keV}$, $E_{\beta}^{max} = 546 \text{ keV}$ for 90 Sr, $E_{\beta}^{mean} = 927 \text{ keV}$, $E_{\beta}^{max} = 2279 \text{ keV}$ for 90 Y). Experimental beta acquisition for both BC-404 and MOF-205 are represented in **Figure 2.B-D** with their respective simulated detection efficiency. MCNP6.2 simulation stops at the particle-matter interaction and energy deposition, so do not simulate any luminescence phenomenon nor any light propagation. Therefore, similar simulation spectra may lead to different experimental spectra, with discrepancies originating from light generation and propagation. As shown, going from low-energy emitter 60 Co to a

260	higher energy emitter ³⁶ Cl led to an increasing response in channels, thus in deposited energy.
261	However, comparing ³⁶ Cl spectrum with a much higher energy emitter such as ⁹⁰ Sr/ ⁹⁰ Y, no
262	important change of the spectrum was noticed. This is not surprising considering the high-
263	energy 90Sr beta particles compared to the size of the pellet. Simulated detection efficiency
264	(Inset of Figure 2.D) confirms that the generation of less photons comes therefore from a partial
265	energy deposition within the pellet, as both energy deposition spectra are similar in shape and
266	intensity.
267	Moving on to gamma detection possibility, and knowing that the geometry of our scintillators
268	is not ideal for such detection (which requires large detector volume in general), several
269	scintillation spectra were recorded using low-energy gamma emitter such as ²⁴¹ Am
270	$(E_{\gamma} = 59.5 \text{ keV } (36.9\%), \text{ Figure 2.E}) \text{ and } ^{133}\text{Ba} (E_{\gamma} = 81 \text{ keV } (33.3 \%) \text{ and } 356 \text{ keV } (62.0 \%),$
271	Figure S6), and compared to simulation. To avoid the possible ²⁴¹ Am alpha interaction, a thin
272	layer of paper was placed between the source and the detector. Simulation shows (Inset of
273	Figure 2.E) a noticeable 59.5 keV full absorption peak (PE) that is observable only for MOF-
274	205 due to its higher density than BC-404. Experimentally, this was partially confirmed as BC-
275	404 and MOF-205 spectra showed scintillation response discrepancies. BC-404 is composed of
276	a Compton edge (CE) whereas MOF-205 is composed of a unique Gaussian-type spectrum. We
277	expect that it is a convolution of CE and PE with the corresponding maximum attributed to the
278	59 keV gamma ray. As the considered energy is low and therefore near to the background noise,
279	we used a coincidence assembly to go deeper in our interpretation. Comparison between forms
280	of both spectra (Figure S7) also shows discrepancy. The fact that there are two patterns for
281	MOF-205 is in agreement with our above explanation. So far, the best explanation is that due
282	to the poor resolution of our measurement chain, it is not possible to correctly separate the
283	Compton edge from the PE. Instead, we have a convolution of both corresponding distributions.
284	This trend was also observed for ¹³³ Ba (Figure S8). Contrary to the ²⁴¹ Am configuration it is
285	possible to distinguish two contributions. We hypothesized a probable 356 keV full absorption 11

peak but it was difficult to investigate and no formal conclusion was drawn even after 10 million
pulses recorded. We estimate that the first visible maximum around channels 1900 corresponds
to the 81 keV full absorption peak. By comparing the channels between ²⁴¹ Am and ¹³³ Ba, these
contributions seem to correspond to the two emitted gamma at 81 keV and 356 keV confirming
the above hypothesis. To the best of our knowledge, the observation of PE in MOF was never
achieved yet and we believe that this was possible in this study due to increased densification.
Considering both simulation and experimental data, it was possible to establish a calibration
curve by making a parallel with $^{244}\mathrm{Cm}$ alpha spectrum, $^{60}\mathrm{Co}$ and $^{36}\mathrm{Cl}$ beta emitters and gamma
emitter such as ²⁴¹ Am and ¹³³ Ba. To do so, an energy deposition endpoint for beta distributions
was read as the mean value between the first value that reaches zero and the last. For the specific
alpha emitter ²⁴⁴ Cm, the point was read as the average mean value of the peak. For ²⁴¹ Am and
¹³³ Ba gamma emitters, the point was taken into account only for MOF-205 as it presents a full
absorption peak and it was read at the maximum of the curve endorsed by simulation. Figure
2.F shows the channels versus the corresponding simulated maximum energy deposition for
BC-404 and sintered MOF-205. For BC-404, it is possible to say with confidence that our model
fits well as the trend curve passes through the three points with an R² factor of 0.9998. This
furthers confirms our beta endpoint determination method, which has sufficient precision for
an energy calibration curve. Regarding MOF-205 the model looks consistent with the exception
of ²⁴⁴ Cm. This confirms the previous hypothesis that the auto-quenching for alpha ionization is
more important in the MOF than within the BC-404, which means that the output energy is
lower than the would be perceived 560 keV. It is also important to note that the trend is linear,
even at low energy. However, it is well known that both organic and inorganic scintillator are
not linear with the incident energy, this effect appearing below 100 keV. ^[21] This observation
remains far beyond the scope of this study as the MOF scintillation is still a new field and
requires further exploration to draw consistent conclusions

Having explored the scintillation performances of the sintered MOF-205, we tried to challenge
the material up a bit with the study of its potential discrimination properties. In particular,
alpha/beta and alpha/gamma discrimination were evaluated. It is noteworthy that such
properties are not straightforward for all-purpose scintillators and have never been studied in
MOF scintillation to the best of our knowledge, even if it was hinted by previous results. ^[15]
This discrimination is related to higher ionization densities within the material when the
incoming particle becomes heavier. This lead to a denser population of excited state, causing
increase proximity of triplet state[22] With two neighboring triplet states, annihilation may
occur, thus leading to delayed fluorescence paving the way to discrimination between particles
of different dE/dx. $^{[23]}$ MOFs belong to the class of supramolecules that are keen to perform
triplet-triplet annihilation, [24] thus particle discrimination should be effective if properly
recorded.
As mentioned, two case studies were performed with the same BC-404 and MOF-205 pellets.
First is the alpha/beta discrimination, second is the alpha/gamma discrimination. Due to the
small size of the MOF-205 scintillator compared with our 2.5 cm diameter sources, experiments
were performed sequentially, that is to say alpha then beta or gamma spectra. Figure 3, top
shows the bidimensional spectra of ²⁴⁴ Cm (left), ³⁶ Cl (center) and their addition (right). Since
the tail of alpha-related pulses is slightly longer than beta- or gamma-related pulses, the
integration of the delayed charge over the total charge allows sorting the nature of the excitation
that led to scintillation. Such pellet configuration is favorable for this discrimination as the
scintillator is intrinsically poorly sensitive to gamma rays and alpha emitters see the full
absorption of their energy within the material. But still and as expected, alpha/gamma
discrimination using a gamma-emitting ¹³³ Ba source was also possible (Figure 3, middle). As
a visual comparison, alpha/beta discrimination of BC-404 was less pronounced (Figure 3,
bottom), with the two lobes being tilted with a positive slope for an unknown reason. BC-400,
a close equivalent to BC-404 was found to display moderate α/β discrimination as well. ^[25] . In

addition, a noticeable Figure of Merit (FOM) of 0.55 was calculated over the full spectrum for both α/β and α/γ discrimination (Figure S9). Ultimately, fast neutron/gamma discrimination with MOF-205 was also tested but the results were harsh to interpret, mainly due to the small size of the material.

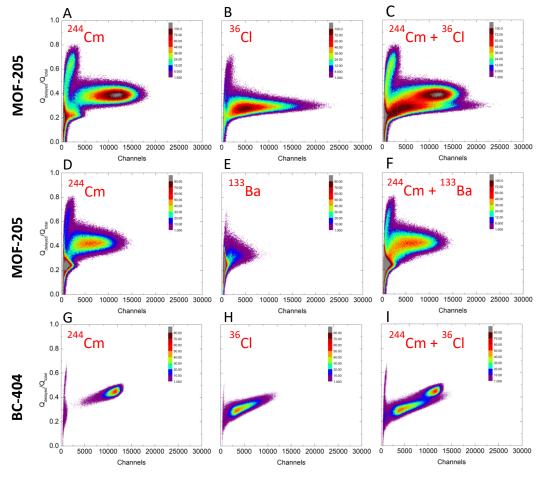


Figure 3. Pulse Discrimination spectra for various configurations. Left: ²⁴⁴Cm. Center: ³⁶Cl or ¹³³Ba. Right: superposition of the two precedent spectra. Note that the two ²⁴⁴Cm spectra for MOF-205 are not identical due to differences in the positioning of the source against the scintillator. See supporting information for full details.

3. Conclusion

In conclusion, an important advancement in scintillating MOFs characterization is presented here. Thanks to sintering process, the access to a key parameter such as the light output is now straightforward if one uses the most appropriate radionuclide (which means alpha or beta emitters) as the excitation. Here we recommend the use of 60 Co or 36 Cl as beta source, since

their energy is fully absorbed by the material and the stopping range is not too elevated. Thus,
a $400\mu m$ thick MOF-205 pellet displayed interesting scintillation properties, an emission
wavelength of 409 nm, a mean decay time of 14.3 ns and a scintillation yield 37% the one of
anthracene. Both alpha, beta and gamma experimental spectra were supported by MCNP6.2
calculations. Our sintered MOF was not fully transparent but the as-prepared pellet was
prepared exclusively from MOF-205, as this was our main goal. Pellets potentially prepared
with diluted MOF-205 with cubic powder of the same refractive index would lead to materials
with better transparency. It is the first time that alpha/beta and alpha/gamma discrimination is
qualitatively acknowledged for a MOF. Finally, this study opens a new and exciting research
topic. First, we guess that sintered transparent MOFs, achieved for the first time in this work,
will be an ongoing and explored field in the next years for optical application mainly. Secondly,
this derivative class of metal organic frameworks constitutes a brand new class of scintillator
full of opportunities. For instance by using the unique versatility of MOFs and by playing on
the composition with heavy metal as nodes and on sintering parameters, we guess that it should
be possible to be more sensitive to some ionization and therefore increase the energy response.
The goal is to be positioned between organic and inorganic scintillators as a new class of hybrid
materials. We hope that this report will be a tremendous input in the field as it brings two new
concept relative to the already rich area of MOF: sintering and scintillation discrimination.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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