Innovative nanocrystal-based scintillators for next-generation sampling calorimeters

M. Soldani[1,*], *A.* Antonelli[1], *E.* Auffray[2], *S.* Brovelli[3,4], *F.* Bruni[3], *M.* Campajola[5,6], *S.* Carsi[7,8], *F.* Carulli[3], *G.* De Nardo[5,6], *E.* Di Meco[1,9], *E.* Diociaiuti[1], *A.* Erroi[3], *M.* Francesconi[6], *I.* Frank[2,10], *S.* Kholodenko[11], *N.* Kratochwil[2], *E.* Leonardi[12], *G.* Lezzani[7,8], *S.* Mangiacavalli[7,8], *S.* Martellotti[1], *M.* Mirra[6], *P.* Monti-Guarnieri[13,14], *M.* Moulson[1], *D.* Paesani[1,9], *E.* Paoletti[1], *L.* Perna[7,8], *D.* Pierluigi[1], *M.* Prest[7,8], *M.* Romagnoni[15,16], *A.* Russo[1], *I.* Sarra[1], *A.* Selmi[7,8], *F.* Sgarbossa[17,18], *R.* Tesauro[1], *G.* Tinti[1], and *E.* Vallazza[8]

[1]INFN Laboratori Nazionali di Frascati, Frascati, Italy
[2]CERN, Meyrin, Switzerland
[3]Università degli Studi di Milano Bicocca, Milan, Italy
[4]Glass to Power SpA, Rovereto, Italy
[5]Università degli Studi di Napoli Federico II, Naples, Italy
[6]INFN Sezione di Napoli, Naples, Italy
[7]Università degli Studi dell'Insubria, Como, Italy
[8]INFN Sezione di Milano Bicocca, Milan, Italy
[9]Università degli Studi di Roma Tor Vergata, Rome, Italy
[10]Ludwig-Maximilians-Universität München, Munich, Germany
[11]INFN Sezione di Pisa, Pisa, Italy
[12]INFN Sezione di Roma, Rome, Italy
[13]Università degli Studi di Trieste, Trieste, Italy
[14]INFN Sezione di Trieste, Trieste, Italy
[15]Università degli Studi di Ferrara, Ferrara, Italy
[16]INFN Sezione di Ferrara, Ferrara, Italy
[17]Università degli Studi di Padova, Padua, Italy
[18]INFN Laboratori Nazionali di Legnaro, Legnaro, Italy

Abstract. The design of next-generation calorimeters for accelerator-borne experiments at the intensity frontier poses unprecedented challenges with regard to timing performance and radiation resistance, while rivaling the current state of the art in terms of energy resolution. A significant role may be played by quantum dots, i.e., light-emitting semiconductor nanocrystals with high quantum yield and rather easy to manufacture. Quantum dots can be cast into an optically transparent polymer matrix to obtain nanocomposite scintillators, which are functionally similar to conventional plastic scintillators and can feature O(100 ps) emission times and O(1 MGy) radiation resistance. Moreover, they are rather economical, thus suiting large-volume applications. The NanoCal project is evaluating the potential for the use of perovskite-based nanocomposite scintillators in sampling calorimeters, which is nowadays yet to be extensively explored. We are performing comparative tests of innovative scintillators, both fully organic and nanocomposite, as standalone samples and integrated in fine-sampling shashlik calorimeter prototypes. Measurements are performed using both cosmic rays and electron and MIP beams in a wide energy range (at the CERN and INFN LNF beamtest facilities), allowing the performance gains obtained from the different scintillators to be directly characterised.

1 Introduction

Quantum dots are crystalline structures with a size of O(1 nm). Their interaction properties (e.g., absorption and emission bands, emission time, etcetera) can be engineered by optimising the nanocrystal size, which makes their use in the development of innovative scintillating media potentially appealing. For instance, perovskite (e.g., caesium lead bromide – $CsPbBr_3$) nanocrystals have been found to emit green scintillation light with reasonable yield, decay times down to O(100 ps), and good resistance to radiation up to O(1 MGy) [1].

The nanocomposite (NC) scintillators could meet the performance requirements of various applications in high-energy physics, especially in calorimetry. Indeed, the goal of the NanoCal blue-sky project (AIDAinnova [2] WP 13.5) is to construct the prototype of a sampling calorimeter with NC scintillator and test it with high-energy particle beams.

The shashlik scheme is naturally ideal as a test platform: a very-fine-sampling shashlik prototype can be eas-

*e-mail: mattia.soldani@lnf.infn.it

ily constructed, and both the required primary scintillator and WLS fibres can be optimized using NC technology. The baseline design of our prototypes was developed starting from the one described in [3]: it features 300 μm thick Pb layers interleaved with 1.5 mm scintillator layers, resulting in a sampling fraction of $\sim$ 45%. The towers with transverse size 5.5 cm, with 6×6 fibres passing through a single tower, which form a bundle with a diameter of $\sim$ 1 cm that can be coupled to, e.g., traditional photomultipliers or SiPMs.

The design described in [3] features a molecular scintillator developed at Protvino. It is made with a polystyrene (PS) matrix, which primarily radiates in the UV-A part of the spectrum, and two secondary fluors: 1.5% of p-terhpenyl (PTP), which has an absorption (emission) band peaked around 275 nm (335 nm), and 0.04% POPOP or 1,4-bis(5-phenyloxazol-2-yl) benzene, which shifts the UV light emitted by PS and PTP into the blue band at $\gtrsim$ 400 nm. This scintillator was considered, e.g., for the PANDA [4] and HIKE [5, 6] electromagnetic calorimeters. The light is then collected and transported to the photodetectors via blue-to-green Y-11 WLS fibres produced by Kuraray [7].

One of the objectives of the NanoCal project is a full performance comparison between the scintillator-fibre scheme described above and other combinations featuring innovative scintillators, both NC and entirely molecular. Our first tests focussed on $CsPbBr_3$ nanocrystals dissolved in a UV-cured 80% polymethyl methacrylate (PMMA), 20% polylauryl methacrylate (PLMA) matrix at different concentrations, ranging between 0.05 and 0.8% [1]. This choice was inspired by the promising photo- and radioluminescence results discussed in [1]: the observed light yield appeared linear with the quantum dot concentration, reaching a value of 4800 γ/MeV for the 0.8% sample. From a 3-component fit to the pulse shape for the 0.2% sample, more than 30% of the light was seen to be emitted in less than 80 ps, with about 20% emitted with a decay time $\tau \sim 600$ ps, and the rest with $\tau \sim 10$ ns. No decrease in light yield was observed after irradiation with doses of up to 1 MGy.

2 Preliminary tests of shashlik compact modules

In 2023, we tested small ($\sim$ 6 cm thick) shashlik modules with the geometry described above, each read out by a Hamamatsu S13360-6050CS SiPM [8]. Two of the modules were constructed with NC active layers (0.2% w/w $CsPbBr_3$ in PMMA) read out with one type of green-to-orange WLS fibres each, i.e., the commercial Kuraray O-2 [7] and a custom-dyed version, produced by Kuraray as well and labelled NCA-1, that features PS doped with 200 ppm of perylene dyad [9] – these modules are labelled "Mod_1" and "Mod_2" respectively. A geometrically identical module with the conventional blue PS scintillator discussed in the previous section and Kuraray Y-11 fibres was also built ("Mod_0") to provide a benchmark.

Moreover, another module with NC scintillator, labelled "Mod_3", was developed with the idea of minimising the contribution of self-reabsorption of the light by the quantum dots. Instead of using $CsPbBr_3$ only, mixed-halide $CsPb(Br,Cl)_3$ nanocrystals (with about half of the Br atoms substituted with Cl atoms) were used. The resulting quantum dots emit in the blue-violet, so coumarin-6 was introduced to shift the light back to the green light typical of caesium lead bromide for readout with the green-to-orange WLS fibres. The tested modules are shown in figure 1.

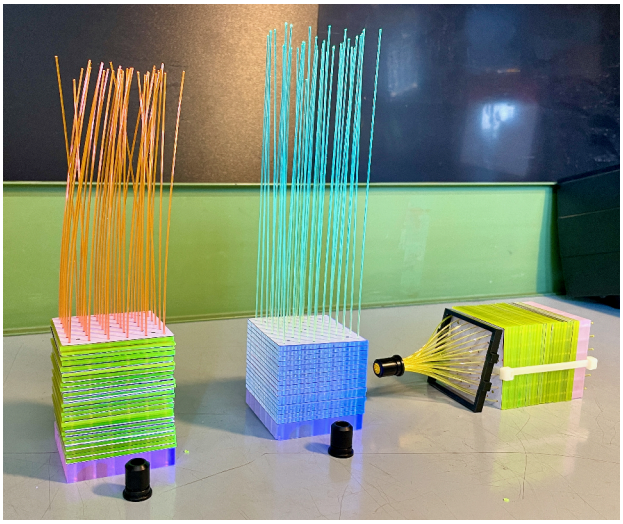

Figure 1: Shashlik modules tested at CERN in 2023. From the left: Mod_2, Mod_0 and Mod_1. At a visual inspection, Mod_3 is qualitatively similar to Mod_1.

Tests of these modules were performed at the T9 beamline of the CERN PS with a 10-GeV/c muon/pion mixed beam. These tests demonstrated that the light yield for single ionising tracks from the prototypes with NC scintillators is in general extremely limited with respect to that from the conventional module (whose response map is shown in figure 2 left) – at the level of a few %. In general, two possible explanations were identified: excess self-absorption by the nanocrystals, and inefficient excitation of the nanocrystals, whether because of their low concentration or because of the lack of an efficient energy transfer mechanism from the (non-aromatic) polymer matrix to the quantum dots.

Interestingly, Mod_3 exhibited poor performance as well. As shown in figure 2 right, very little signal is observed from energy deposit in the prototype, the only evident exception being the case of tracks impinging directly on the WLS fibres, either inside the module (array of small dots spaced by $\sim$ 1 cm in the plot) or downstream of it, where the fibre bundle is coupled to the SiPM (big spot at the centre with a diameter of $\sim$ 1 cm). The reason for the limited performace is that the surface passivation of the nanocrystals was damaged during the substitution reaction, leading to crystal aggregation in the NC that in turn resulted in a milky appearance and poor transparency. However, the concept remains interesting and should be tested again, especially with direct synthesis of

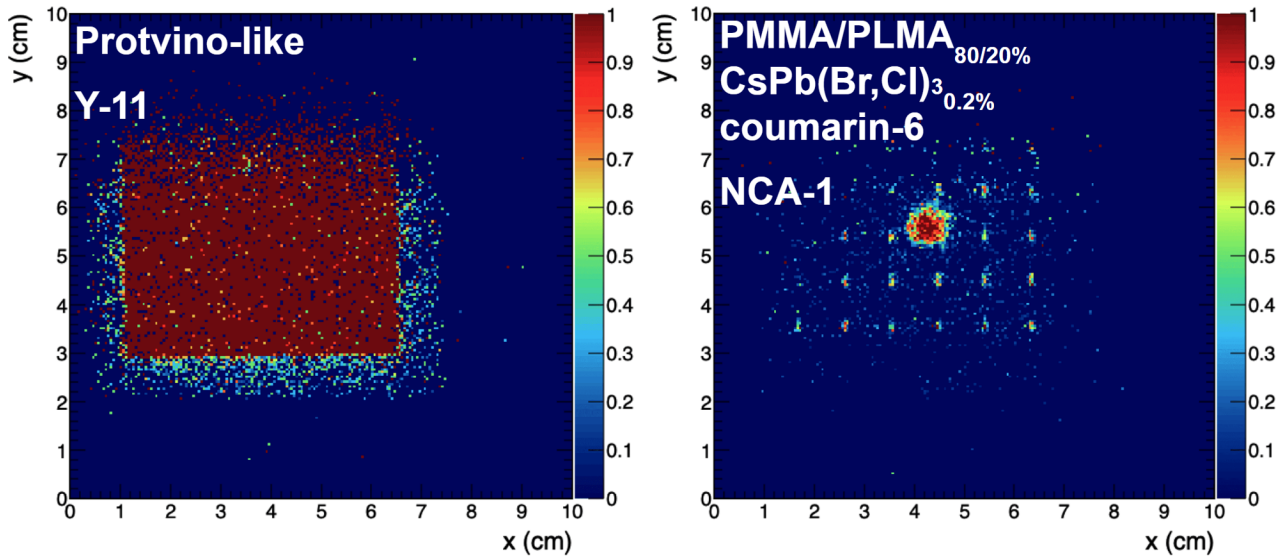

Figure 2: Map of the response of Mod_0 *(left)* and Mod_3 *(right)* to $O(10\ \mathrm{GeV}/c)$ muons/pions, measured at the CERN T9 beamline in 2023.

the $CsPb(Br,Cl)_3$ nanocrystals to preserve the surface passivation.

3 Measurements at the INFN LNF BeamTest Facility

In order to separate the evaluation of the scintillating media alone from other components related to, e.g., the calorimeter geometry and the light transfer from the active layers to the WLS fibres, we focussed on testing small sample of scintillator directly coupled to a photodetector. In particular, between late 2023 and early 2024 we prepared several cylindrical samples (14.3 mm ∅, 6.7 mm thick) to be directly coupled to an S13360-6050CS SiPM.

All the samples feature an aromatic matrix made of 90% polyvinyl toluene (PVT) and 10% divinylbenzene (DVB). This has been rendered possible improving the protocols for the synthesis of thermally polarised perovskite-based NC materials, which has proven necessary since PVT cannot be photopolymerised. This polymer provides a mechanism for energy transfer from the matrix to the quantum dots via the primary scintillation light from the aromatic rings.

Table 1 lists all the samples produced in two batches – in Fall 2023 and in Winter 2024. Three baseline samples were made available: two commercially available scintillators by Eljen, i.e. EJ200 (general purpose, with a scintillation efficiency of $10^4\ \gamma/1\text{−MeV}{-}e^-$) [10] and EJ232Q quenched by 0.5% benzophenone (optimised for fast emission, with efficiency 2900 $\gamma/1\text{−MeV}{-}e^-$ and decay time 700 ps) [11], and one similar to the PS-based scintillator described in section 2 and in [3] (“Mol_0”). “Mol_1/2/3” are innovative molecular compositions. All the NC samples feature fluorine-coated $CsPbBr_3$ quantum dots. They are divided into two subcategories, based on the colour: the orange samples were obtained by adding the green-to-orange WLS perylene dyad to the green solutions.

All these scintillators were probed with a 450-MeV single-electron beam at the Frascati BeamTest Facility (BTF) in April 2024. Blank_1 (0) gives about 20% (7%) of the light output of EJ200, which provides a baseline for the activity of the components of the NC and test setup other than the perovskite itself. Adding the perylene dyad to either blank does not change its light output. So, any absorption of light from the matrix or from the PTP by the perylene is compensated by the re-emission of light from it. The absorption of light by the perylene is thus small, because if a large fraction of the primary light were absorbed/re-emitted by the perylene, a small reduction of the overall response due to the decreased sensitivity of the SiPM at longer wavelengths would be observed. Mol_0 gives about 50% of the light output of EJ200, and EJ232Q about 33%. Mol_3, a green scintillator, gives a light output that is similar to that of Mol_0.

NC24_0/1 give about 64% of the light output of Blank_0: adding the quantum dots seems to lower the light output with respect to that of the matrix alone. The same effect is seen among the samples with PTP, which appears to play an important role in transferring the deposited energy from the matrix to the perovskite absorption band or directly to the SiPM sensitivity band. In general, the fact that adding the nanocrystals decreases the light output suggests that the perovskite is heavily absorbing its own (green) light, in addition to the (UV/blue) light from PTP.

Adding the perylene dyad restores some of the light output in case of both samples NC23_1 and NC24_4, increasing it by about 20% relative to the corresponding samples without perylene, i.e., NC23_0 and NC24_2 respectively. This is consistent with the hypothesis that self-absorption by the perovskite plays a significant role in reducing the yield: with perylene, at least some of the light is shifted to longer wavelengths before self-absorption.

Albeit from different batches, which where produced with different passivation procedures and synthesis pro-

Name	Batch	Composition	Colour	Notes
Blank_0	2024	Only matrix	–	Blank for NC24_0 and NC24_1
Blank_1	2024	1.5% PTP	–	Blank for NC23_0 and NC24_2
Blank_2	2024	perylene dyad	–	Blank for NC24_3
Blank_3	2024	1.5% PTP + perylene dyad	–	Blank for NC23_1 and NC24_4
EJ200	2024	Proprietary	Blue	Commercial reference [10]
EJ232Q (0.5%)	2024	Proprietary	Blue	Commercial reference [11]
Mol_0	2023	1.5% PTP + 0.04% POPOP	Blue	Cfr. [3]
Mol_1	2023	1.5% PTP + 0.04% benzotiophene	Blue	
Mol_2	2023	1.5% PTP + 0.04% coumarin-6	Green	
Mol_3	2023	1.5% PTP + 0.04% benzotiophene + 0.04% coumarin-6	Green	
NC23_0	2023	1.5% PTP + 1.0% $CsPbBr_3$	Green	
NC23_1	2023	1.5% PTP + 1.0% $CsPbBr_3$ + perylene dyad	Orange	
NC24_0	2024	1.0% $CsPbBr_3$	Green	
NC24_1	2024	2.5% $CsPbBr_3$	Green	
NC24_2	2024	1.5% PTP + 1.0% $CsPbBr_3$	Green	Similar to NC23_0
NC24_3	2024	1.0% $CsPbBr_3$ + perylene dyad	Orange	
NC24_4	2024	1.5% PTP + 1.0% $CsPbBr_3$ + perylene dyad	Orange	Similar to NC23_1

Table 1: Scintillating samples tested at the Frascati BTF. All percentages are w/w.

tocols, NC23_0 and NC24_2 feature the same composition. However, they give very different charge values. The same considerations apply to NC23_1 and NC24_4. Thus, adding the perovskite seems to have lowered the light yield by a larger factor in the second batch than in the first. Indeed, in case of the NC23_0 and 1 samples, some of the perovskite precipitated out on one face of the sample. When this face is coupled to the SiPM, the yield is lower than when the precipitate layer is not in contact with SiPM, which constitutes further evidence that the perovskite self-absorption is blocking part of the light output.

4 Conclusions

Extensive work is ongoing to optimise the use of $CsPbBr_3$ quantum dots to develop high-performance scintillators for high-energy physics. Among the critical points highlighted so far are the important contribution of the nanocrystal self-absorption and the need for enhanced control over the production procedures that guarantee performance reproducibility. On the other hand, some of the molecular solutions probed so far appear promising. We intend to study the emission speed and radiation resistance of Mol_3 in comparison to those of other commercial green scintillators.

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