Innovative **nanocrystal-based scintillators** for next-generation **sampling calorimeters**

CALOR 2024

Tsukuba
つくば市

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on behalf of the NanoCal project

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AIDA innova

drive

next-generation **scintillating calorimeters** at the **intensity frontier** demand

- faster response
- higher radiation resistance
- reasonable light output

than currently available

inorganic (crystals)

- ↗ high-*Z* → homogeneous calorimeters
- ↘ typically slow > ns, up to μs & tradeoff between LY and timing
- ↘ many technological challenges (growth, machining, support…)
- ↘ expensive
- ↘ LY depends on temperature $O(\%/°C)$

organic (plastic)

- ↘ low density and *Z*
- ↗ fast response $\lesssim$ ns
- ↗ easy to handle and scale
- ↗ comparatively easier to craft
- ↗ comparatively cheaper

⇒ ideal active medium in sampling calorimeters

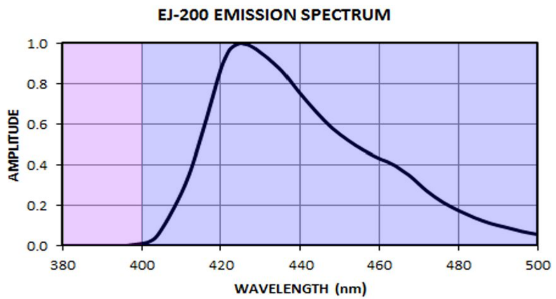
state-of-the-art plastic scintillators

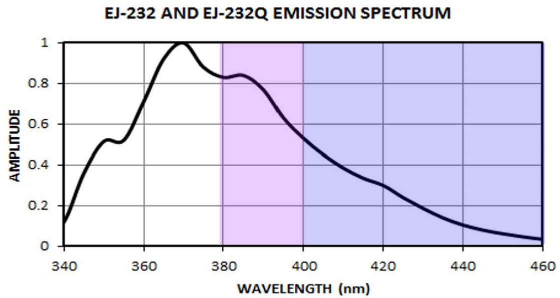
Eljen EJ200

- PVT matrix
- long optical attenuation length 380 cm
  ⇒ good LY 10k ph/MeV
- rather fast 2.1 ns

Eljen EJ232Q

- PVT matrix
- optimised for ultra-fast response 700 ps
- shorter attenuation length 10 cm
- worse LY 2.9k ph/MeV

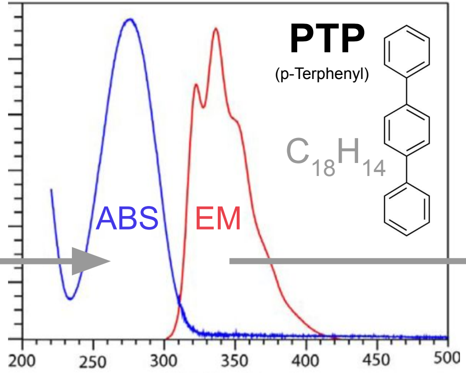


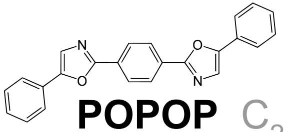


Protvino
PS + PTP$_{1.5\%}$ + POPOP$_{0.04\%}$

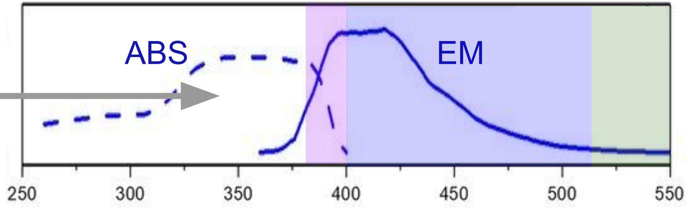
e.g. Singh *et al* **arXiv**:1704.02713

PS
UV-A @ 330 nm





POPOP $C_{24}H_{16}N_2O_2$



overall: emission in UV-A/blue

the **NanoCal** project

aim develop new high-performance **nanocomposite (NC)** scintillators

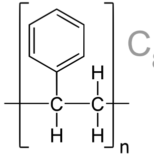
take the best of two worlds:

polymeric matrix with addition of quantum dots

semiconductor nanocrystals
emission properties e.g.
- absorption/emission wavelengths
- emission time

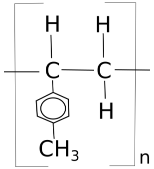
depend on the (tunable) size *O*(1-10 nm)

Poly**S**tyrene



C_8H_8

Poly**V**inyl **T**oluene

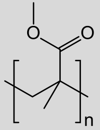


$CH_3C_6H_4CH{=}CH_2$

thermal polymerisation only!

emission: UV-A

Poly**M**ethyl **M**eth**A**crylate



$C_5H_8O_2$

⇒ no emission from the matrix

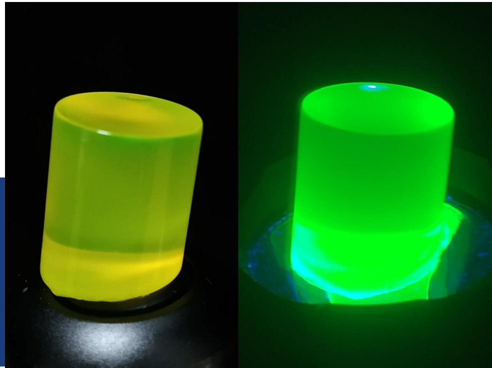
⇒ new primary emission components

⇒ additional WLS to avoid reabsorption by the matrix

⇒ access to larger-wavelength emission
→ less affected by radiation-induced colour centres
rad-hard to *O*(1 MGy)

⇒ overall emission time decrease:
substantial fraction of emission in
O(100 ps)!

e.g. **$CsPbBr_3$**
Cesium Lead Bromide
perovskite
in PVT + PTP



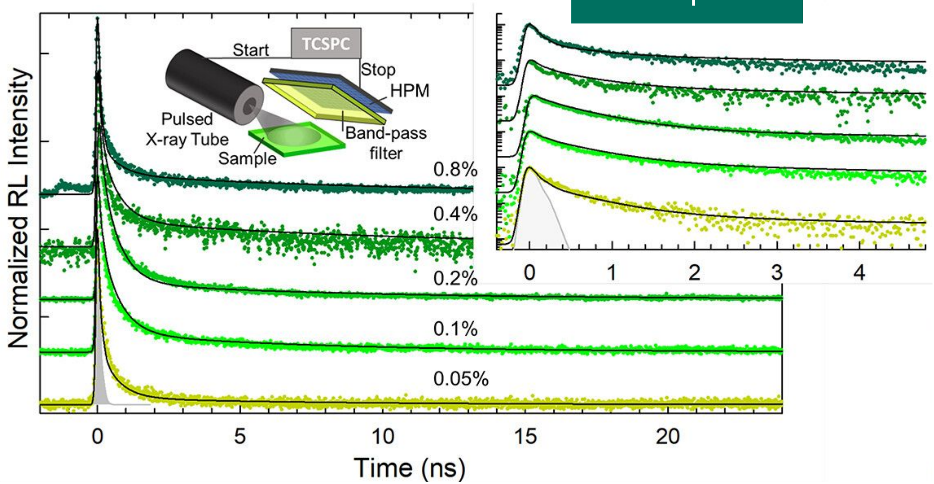
the **NanoCal** project

aim develop new high-performance **nanocomposite (NC)** scintillators

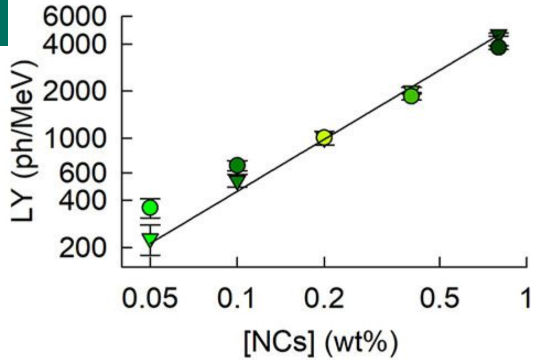
e.g. **$CsPbBr_3$**
Cesium Lead Bromide
perovskite
in PMMA/PLMA

the premise:

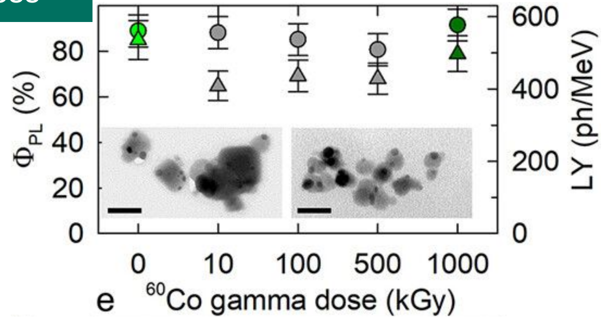
signal development



RL LY



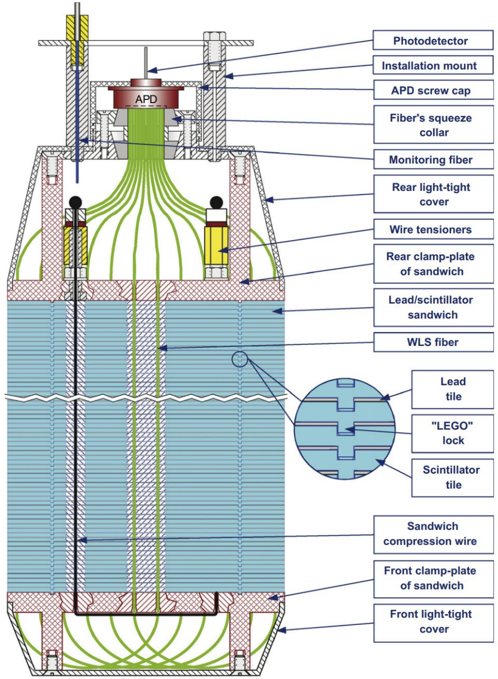
radiation hardness



Erroi *et al* **ACS Energy Lett.** 2023, 8, 3883

the **NanoCal** project

aim application in **fine-sampling calorimeters** → <u>better performance</u> at <u>reduced cost</u>



benchmark

PANDA Singh *et al* **arXiv**:1704.02713

KOPIO Atoian *et al* **arXiv**:0709.4514

shashlik calorimeter

- Pb (275 μm) + PS-based scintillator (1.5 mm)
  ⇒ sampling fraction ~47%
- scintillator:
  PS + $PTP_{1.5\%}$ + $POPOP_{0.04\%}$
  from Protvino
- WLS fibres: Kuraray Y-11(200)
- APD-based readout
- overall prototype resolution:

$$\sigma_E/E = (1.96 \pm 0.1)\% \oplus (2.74 \pm 0.05)\%/\sqrt{E\,(\mathrm{GeV})}$$

$$\sigma_T = \frac{(72 \pm 4)\,\mathrm{ps}}{\sqrt{E\,(\mathrm{GeV})}} \oplus \frac{(14 \pm 2)\,\mathrm{ps}}{E\,(\mathrm{GeV})}$$

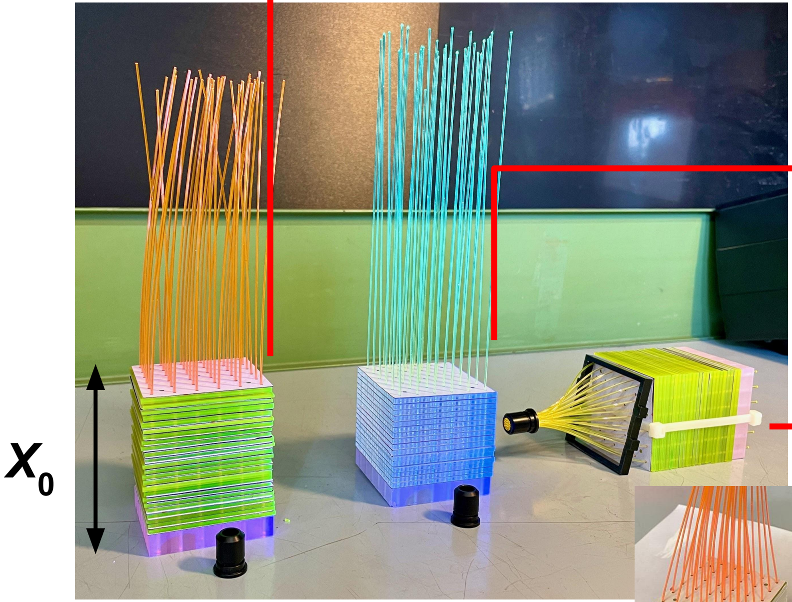
our (current) **concept**

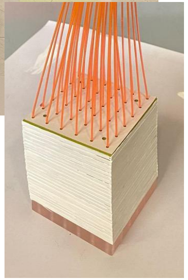
- 300 μm Pb ⇒ sampling fraction ~45%
- scintillator: testing molecular and NC options…
- scintillator-dependent WLS fibres
- different readout choices
  - → SiPMs
    e.g. Hamamatsu S13360-6050CS
  - → wide-range PMTs
    e.g. Hamamatsu R7600U series

⇒ currently testing 1 X_0 single towers…

towards an operational shashlik…

⇒ first unit module generation, built and tested in Spring 2023





PMMA/PLMA$_{80/20\%}$ + $CsPbBr_3$$_{0.2\%}$

custom NCA-1 fibres*

PVT/DVB$_{90/10\%}$ + benzothiophene$_{.04\%}$

Kuraray Y-11(200) fibres

PMMA/PLMA$_{80/20\%}$ + $CsPbBr_3$$_{0.2\%}$

Kuraray O-2(100) fibres

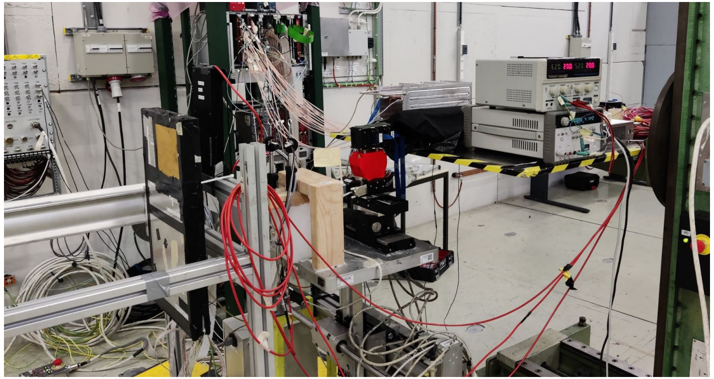
PMMA/PLMA$_{80/20\%}$ + $CsPb(Br,Cl)_3$$_{0.2\%}$ + coumarin-6

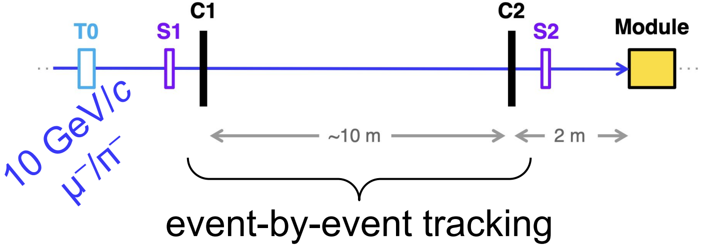
custom NCA-1 fibres*

* from Kuraray, with 200 ppm perylene dyad

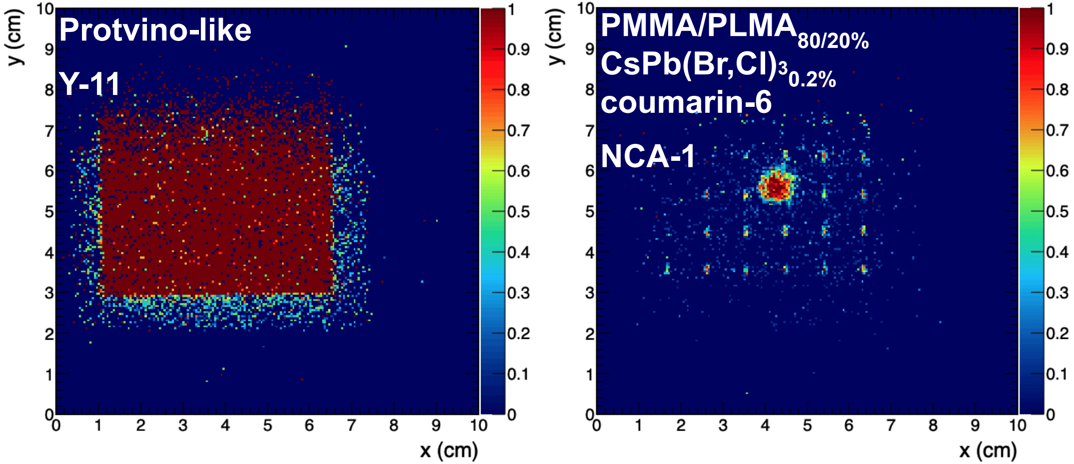
Jun 2024 @ CERN T9

preliminary module tests





aim characterise the performance of all the shashlik unit modules with electrons and MIPS



⇒ excellent performance of the reliable combo of Protvino-like scintillator and Y-11 fibres

⇒ only detectable signal from the NC-based modules comes from the fibres
- PMMA matrix, no PTP, low perovskite concentration
  → insufficient matrix-nanocrystal energy transfer
- reabsorption by the nanocrystals

more investigation is needed!

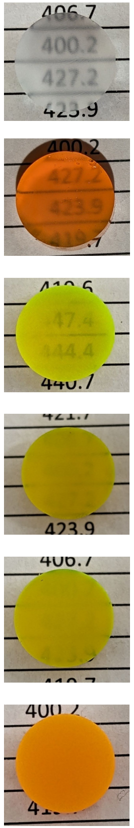
let’s take one step back

our nanocomposite samples produced @ UniMiB

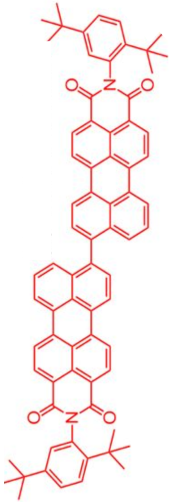
$PVT/DVB_{90/10\%}$ + PTP_{α} + $\gamma^{*}:CsPbBr_{3\,\beta}$ + perylene $dyad_{\delta}$ †

	α	β	γ*	δ	optical features (visual inspection)
Blank_0	0	0	-	0	transparent, colourless
Blank_1	1.5%	0	-	0	transparent, colourless
Blank_2	0	0	-	> 0	transparent, orange
Blank_3	1.5%	0	-	> 0	transparent, orange
NC23_2	1.5%	1.5%	Yb	0	a bit opaque, green
NC23_4	1.5%	1.5%	Yb	>0	a bit opaque, orange
NC24_0	0	1.5%	F	0	opaque, green
NC24_1	0	2.5%	F	0	very opaque, green
NC24_2	1.5%	1.5%	F	0	opaque, green
NC24_3	0	1.5%	F	>0	very opaque, orange
NC24_4	1.5%	1.5%	F	>0	very opaque, orange

- surface passivation to allow use of perovskite in thermally polymerised matrix

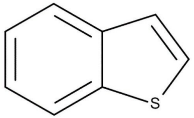


† $C_{20}H_{12}$



our molecular samples produced @ UniMiB

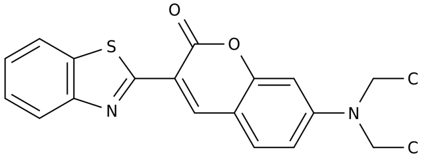
also studying innovative fully molecular recipes



works between matrix and PTP

C_8H_6S

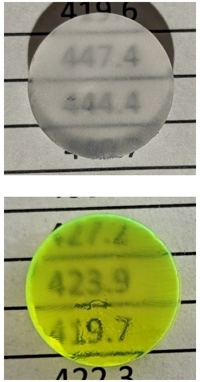
$C_{20}H_{18}N_2O_2S$

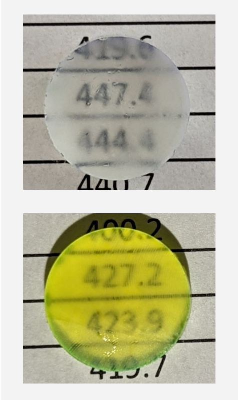


450 nm → 500 nm

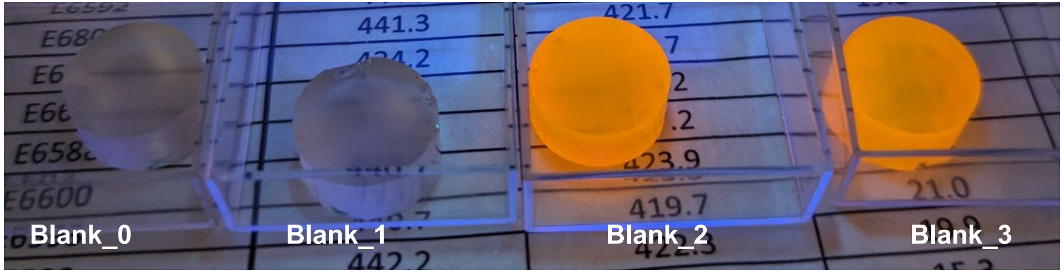
PVT/DVB$_{90/10\%}$ + PTP$_\alpha$ + benzothiophene$_\beta$ + coumarin-6$_\gamma$

	α	β	γ	optical features (visual inspection)
Mol_0 Protvino-*like* with PVT instead of PS	1.5%	0 but POPOP$_{0.04\%}$	0	transparent colourless, **blue** under UV
Mol_1	1.5%	0.04%	0	transparent colourless, **blue** under UV
Mol_2	1.5%	0	0.04%	transparent, **green**
Mol_3	1.5%	0.04%	0.04%	transparent, **green**

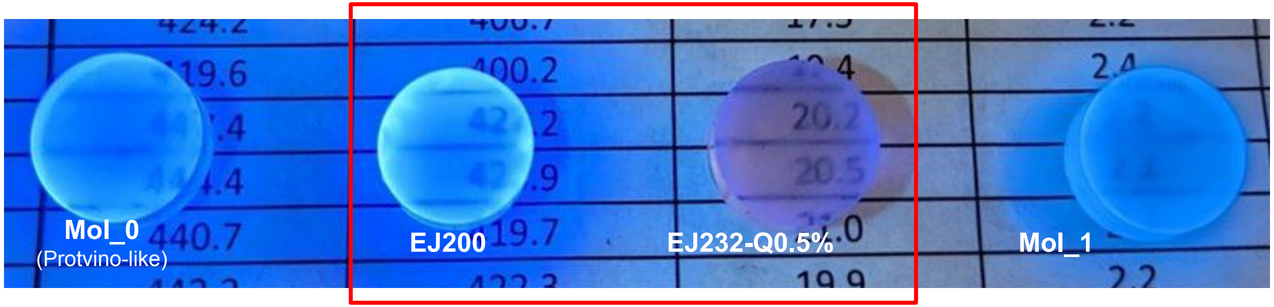


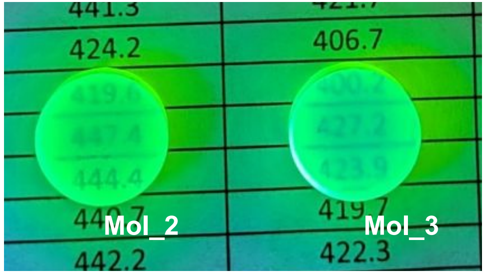


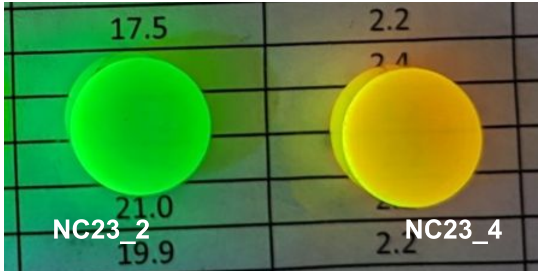
under UV light

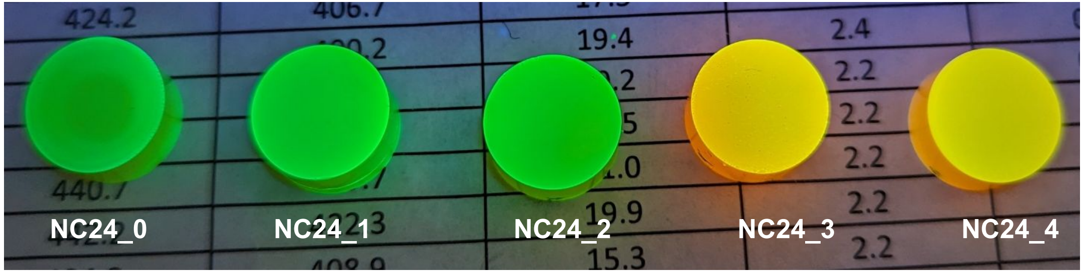


commercial reference





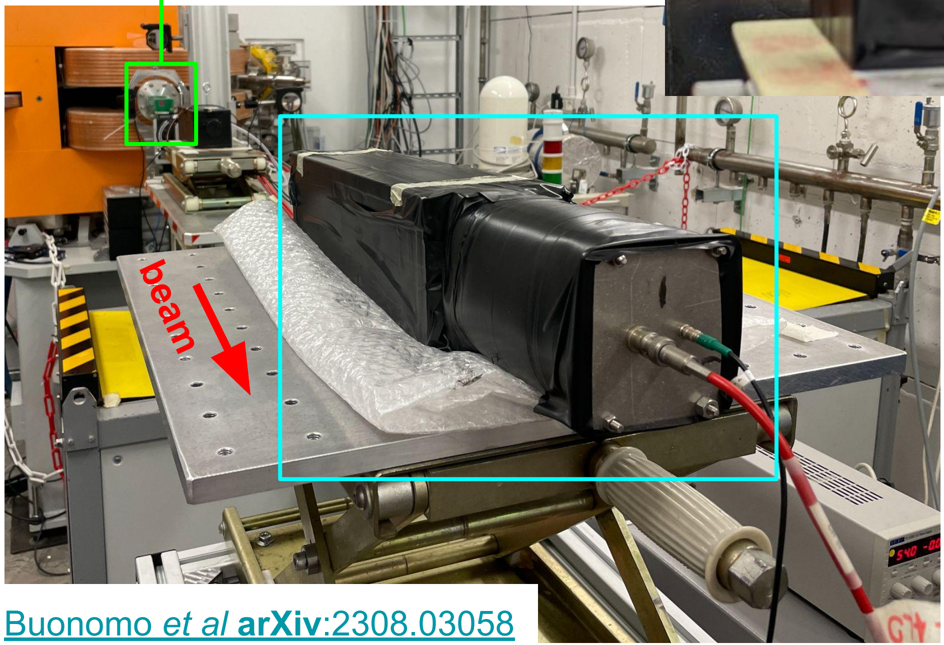




Apr 2024 @ LNF BeamTest Facility

latest measurements

aim to measure the single-particle light output of all our samples



Buonomo *et al* **arXiv**:2308.03058

PROBE

450 MeV electrons, spot size ~400 μm

SETUP

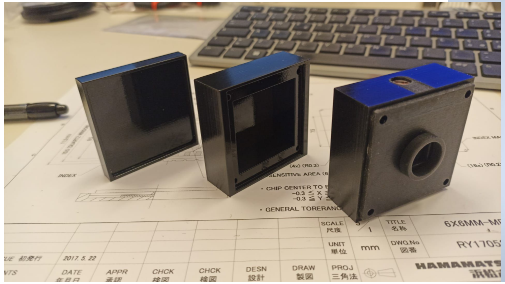
FitPix unit and **Pb glass block** to measure electron multiplicity

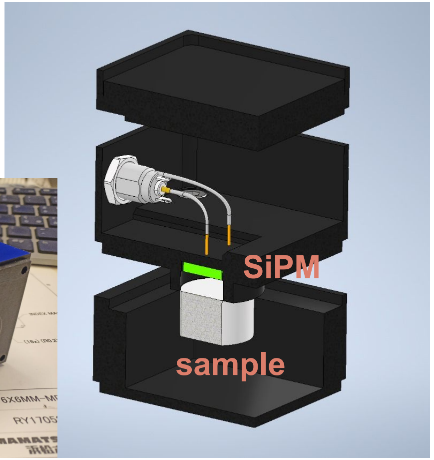
⇒ single-particle selection

TEST DEVICE

- sample (6.7 mm thick, 14.3 mm ∅) coupled to SiPM (Hamamatsu S13360-6050CS) w/ surface index matching
- TIA gain G = 4.87

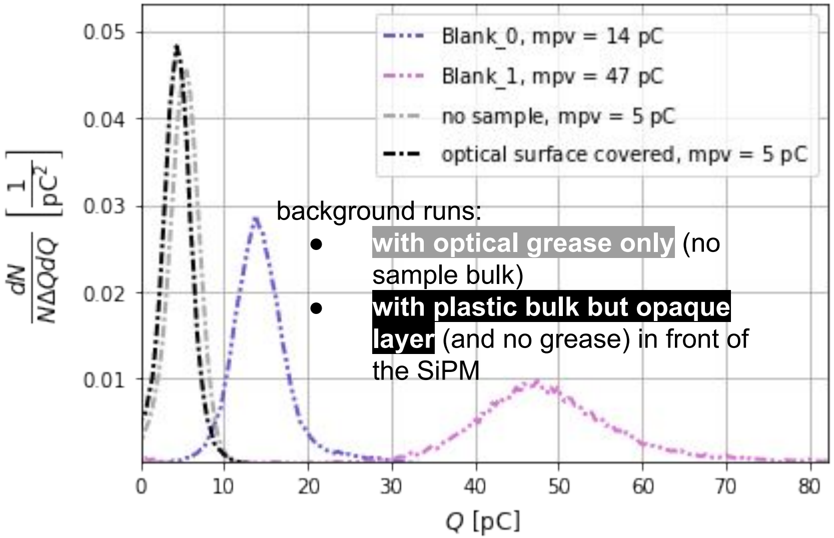
$$Q = \frac{1}{Z_{\text{in}}G}\int V_{\text{out}}(t)\text{d}t$$





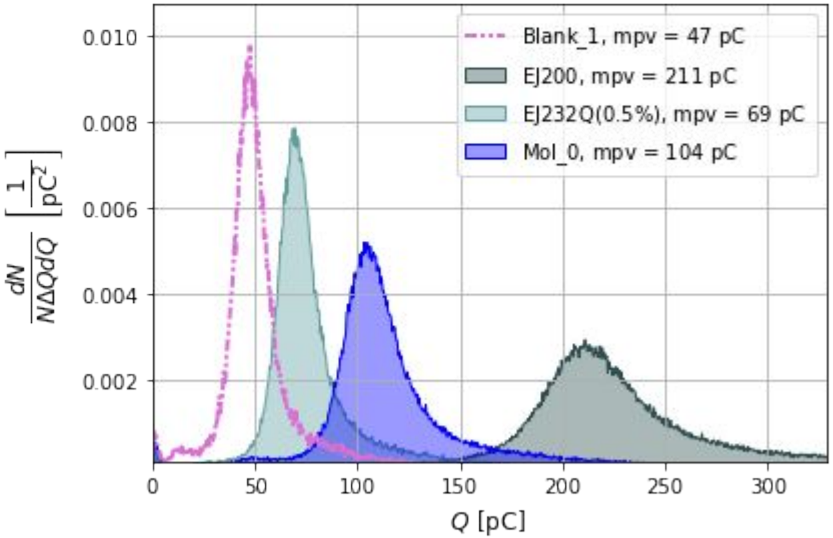
single-electron spectra

background & matrix



- signal from **PVT alone** differs from that obtained in background runs
  - ↘ PVT emission large-λ tail in SiPM range
  - ↘ Cherenkov component
- significant light emitted (> 300% PVT only) by the **PTP-doped matrix**

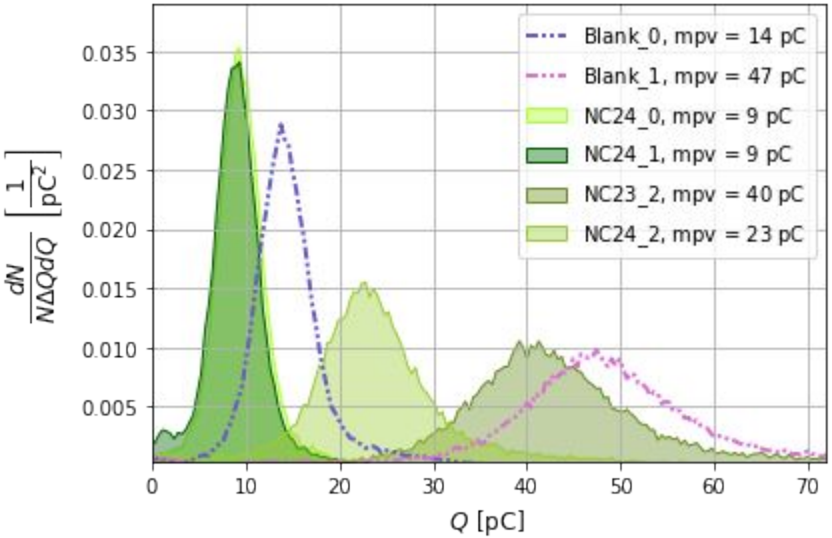
reference



- LY ratio between **EJ200** (datasheet: 10k ph/MeV) and **EJ200Q** (datasheet: 2.9k ph/MeV) correctly reproduced
- **Protvino-like** sample is competitive

single-electron spectra

perovskite unshifted



recall that

NC23_2 and **NC24_2** feature the same recipe (but different quantum dot passivation and different NC batch)

- LY is overall low – always lower than **Blank_1**
  → perovskite seems to block part of the light emitted by the (PTP-doped) matrix
- without PTP, the LY with perovskite is significantly below that of **PVT-only**
  → no light, regardless of the nanocrystal concentration
- **NC24_2** performs more poorly than **NC23_2**

→ although concentration is the same, **NC23_2** appears to be overall more transparent, albeit non uniformly

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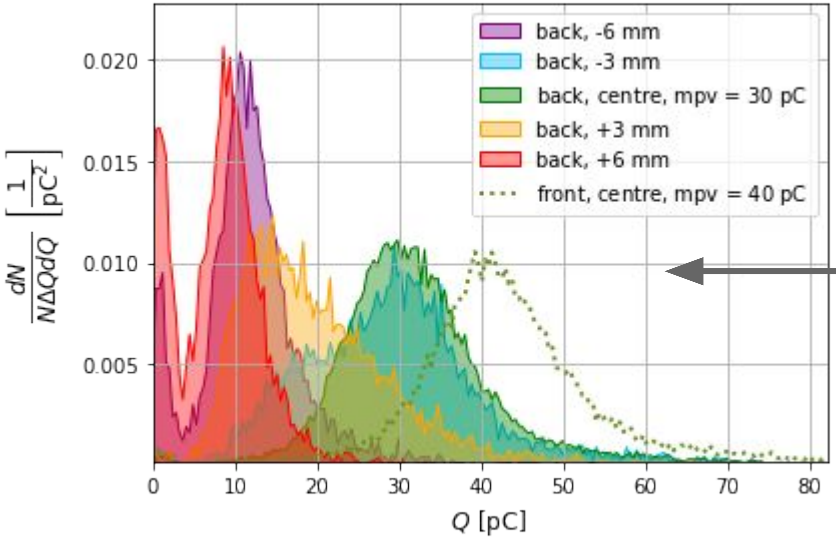
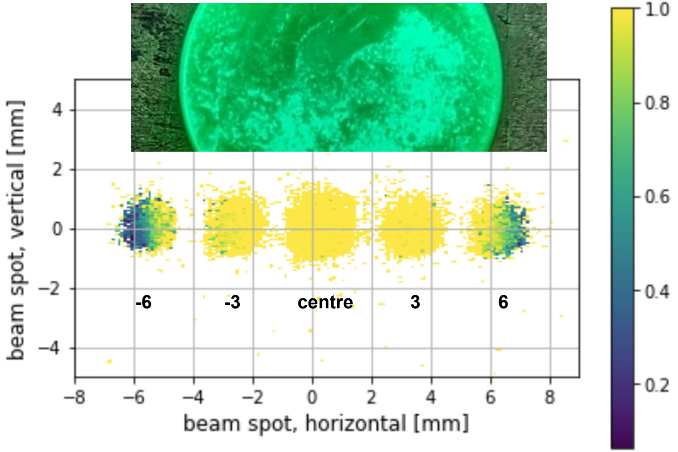
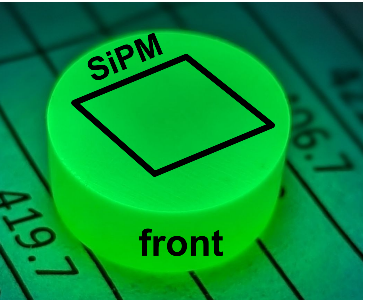
single-electron spectra

perovskite unshifted







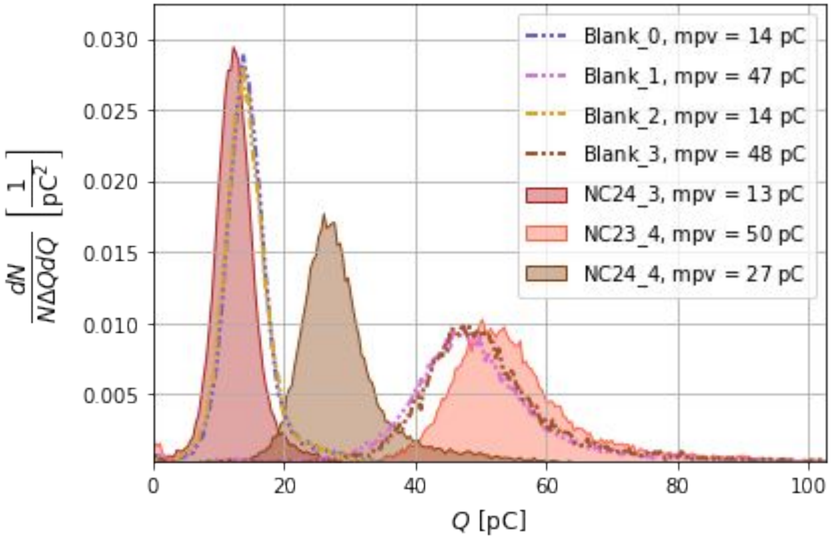
inhomogeneous optical properties ⇐ inhomogeneous distribution of nanocrystals

→ front-back LY asymmetry

→ spatial dependence

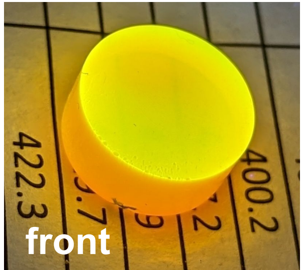
single-electron spectra

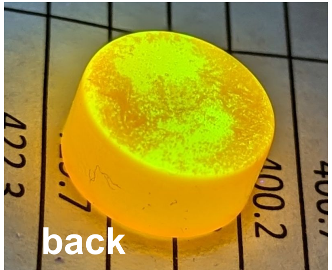
perovskite + perylene



recall that
NC23_4 and **NC24_4** feature the same recipe
(but different quantum dot passivation and
different NC batch)

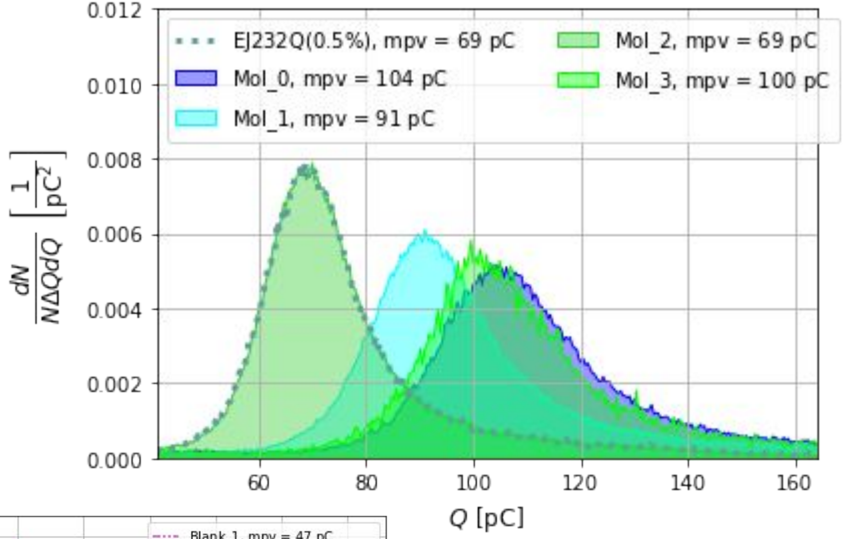
- full matrix+perovskite+perylene (**NC23_4**) performs slightly better than the corresponding **blank**
- **NC24 lot** with perylene has the same issues as the green lot: in both cases, their LY is down to almost 50% that of the **NC23 generation**
- **without PTP**, performance is approximately that of the **sole matrix**
- **Blank_2/3**: perylene does not seem to affect the performance of their counterparts (**Blank0/1**)
- few-% front-back LY asymmetry in **NC23_4**

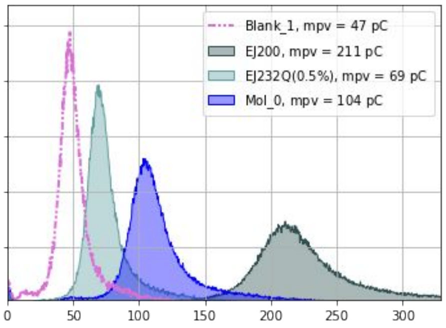




single-electron spectra

molecular





- **Mol_2** (matrix + coumarin-6) is the worst among our fully molecular sample; it attains exactly the same signal distribution as **EJ232Q**
- **Mol_1** (matrix + benzothiophene) features >30% higher LY than **EJ232Q**
- **Mol_3** (matrix + benzothiophene + coumarin-6) performs about like **Mol_0** (Protvino-like), i.e. ~150% **EJ232Q** and ~50% **EJ200**

⇒ very promising!

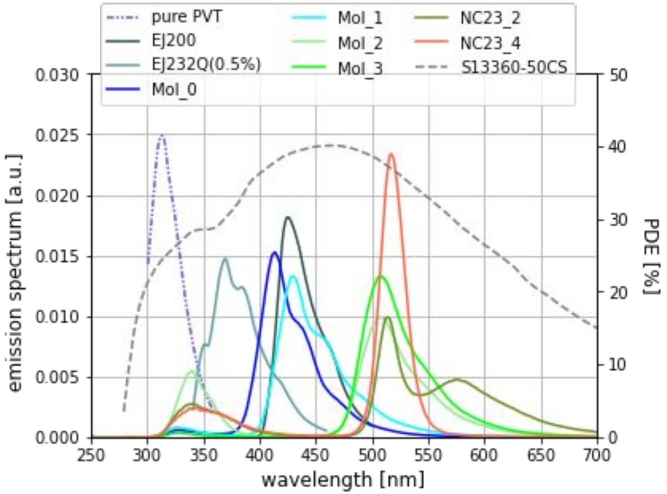
pending evaluation of timing performance and radiation hardness

and there is more…

overall

including

- **emission spectra**, so far measured for the molecular and NC23 sample lots
- **SiPM PDE**



allows for a fair comparison between our most promising samples…

sample	charge MPV [pC]	corr. [% Protvino-like]	charge MPV [pC Protvino-like eq.]	relative LY [% Protvino-like]
Mol_0 Protvino-like	104	100	104	100
EJ200	211	96.5	203.6	194.3
EJ232Q (0.5%)	69	115.3	79.6	75.9
Mol_1	91	97.9	89.1	85.2
Mol_2	69	111.0	76.6	73.0
Mol_3	100	103.1	103.1	99.0
NC23_2	40	106.2	42.5	40.1
NC23_4	50	121.0	60.5	58.0

disappointing results on NC samples in terms of

- overall performance
- consistency between batches

R&D in progress…

promising results from the molecular scintillators, which might be ready for integration in test detectors

the features of nanocomposite scintillators are puzzling: more investigation is needed on
- ↘ the compositions
- ↘ the production techniques

the calorimeter development will naturally follow…

upcoming beamtest Jul 2024 @ LNF BTF

setup optimised for timing measurements
fast T0 reference, fast PMT e.g. Hamamatsu R14755U-100

upcoming beamtest Sept 2024 @ CERN T9

- commissioning of 4-channel, calorimetric-scale module with Protvino-like scintillator purchased from ISMA ⇒ will serve as test bench for photodetectors, fibres, coupling, mechanics
- test of new unit modules based on Mol_3 and perhaps novel NC recipes

plans for 2025

- irradiation tests @ ENEA Casaccia
- dig even deeper into the NC light output mystery

thank you!　　どうもありがとう!

any comments or questions? contact me at *mattia.soldani@lnf.infn.it*!

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supplemental material

the **NanoCal** team

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(common) inorganic scintillators

Parameter:	ρ	MP	X_0^*	R_M^*	dE^*/dx	λ_I^*	τ_{decay}	λ_{max}	$n^\natural$	Relative output†	Hygro-scopic?	$d(LY)/dT$
Units:	g/cm^3	°C	cm	cm	MeV/cm	cm	ns	nm				%/°C‡
NaI(Tl)	3.67	651	2.59	4.13	4.8	42.9	245	410	1.85	100	yes	−0.2
BGO	7.13	1050	1.12	2.23	9.0	22.8	300	480	2.15	21	no	−0.9
BaF_2	4.89	1280	2.03	3.10	6.5	30.7	650^s	300^s	1.50	36^s	no	-1.9^s
							0.9^f	220^f		4.1^f		0.1^f
CsI(Tl)	4.51	621	1.86	3.57	5.6	39.3	1220	550	1.79	165	slight	0.4
CsI(Na)	4.51	621	1.86	3.57	5.6	39.3	690	420	1.84	88	yes	0.4
CsI(pure)	4.51	621	1.86	3.57	5.6	39.3	30^s	310	1.95	3.6^s	slight	−1.4
							6^f			1.1^f		
$PbWO_4$	8.30	1123	0.89	2.00	10.1	20.7	30^s	425^s	2.20	0.3^s	no	−2.5
							10^f	420^f		0.077^f		
LSO(Ce)	7.40	2050	1.14	2.07	9.6	20.9	40	402	1.82	85	no	−0.2
PbF_2	7.77	824	0.93	2.21	9.4	21.0	-	-	-	Cherenkov	no	-
CeF_3	6.16	1460	1.70	2.41	8.42	23.2	30	340	1.62	7.3	no	0
$LaBr_3$(Ce)	5.29	783	1.88	2.85	6.90	30.4	20	356	1.9	180	yes	0.2
$CeBr_3$	5.23	722	1.96	2.97	6.65	31.5	17	371	1.9	165	yes	−0.1

* Numerical values calculated using formulae in this review.

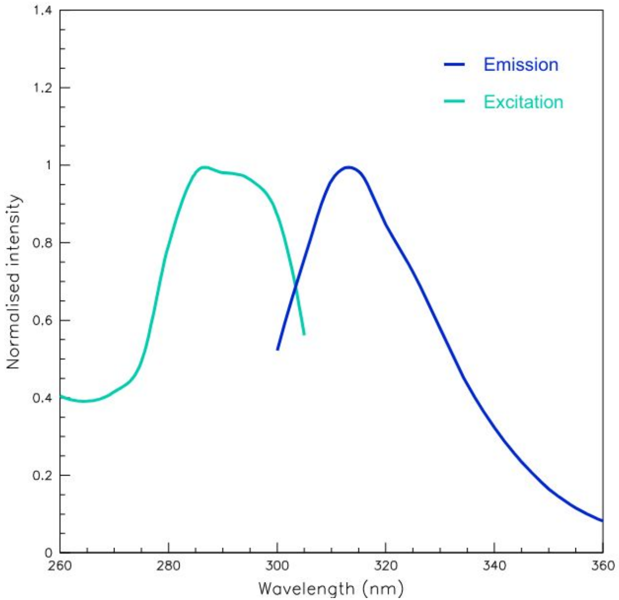
$\natural$ Refractive index at the wavelength of the emission maximum.

$\dagger$ Relative light output measured for samples of 1.5 X_0 cube with a Tyvek paper wrapping and a full end face coupled to a photodetector. The quantum efficiencies of the photodetector are taken out.

$\ddagger$ Variation of light yield with temperature evaluated at the room temperature.

f = fast component, s = slow component

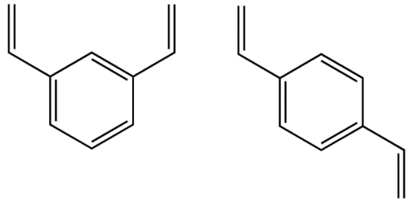
pure PVT spectra



from [Nakamura *et al* **NIM-A** 770 (2015) 131]

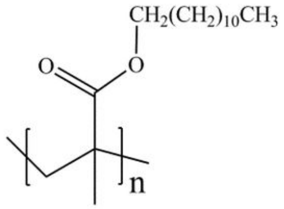
(co)dopants

DiVinylBenzene



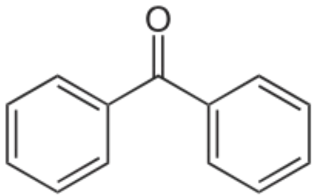
crosslinker: strengthens the matrix

Poly **L**auryl **M**eth**A**crylate



- improves perovskite miscibility
- preserves quantum dot optical features

EJ232 quenching



adding **benzophenone** $C_{13}H_{10}O$ in small amounts (0.5-5%) to the recipe

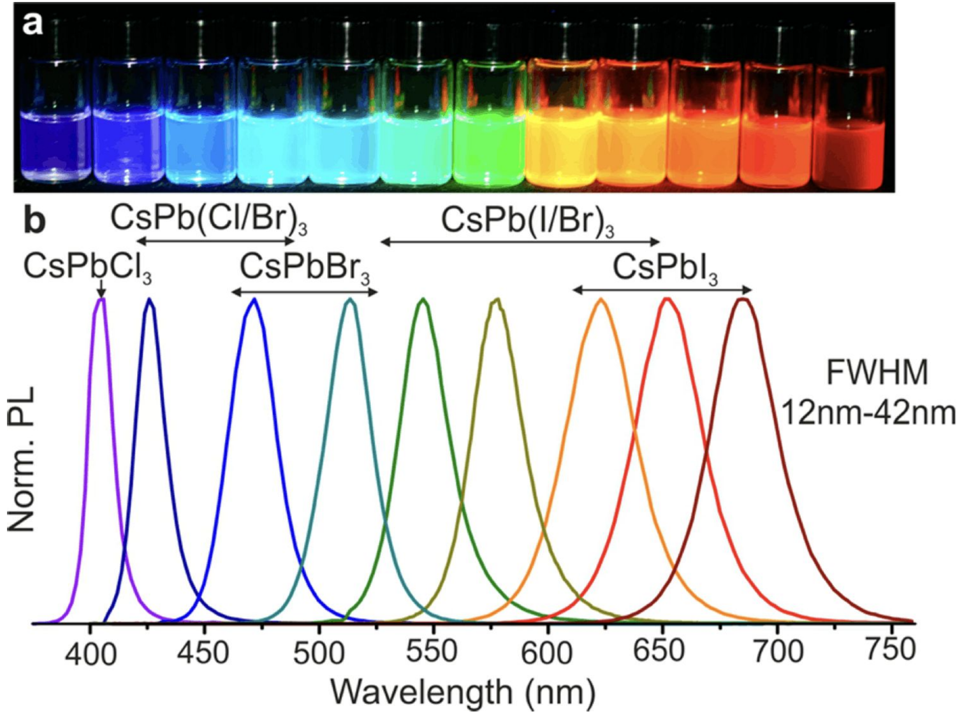
- faster response
- same spectral response

but

- significantly lower LY

PROPERTIES	EJ-232	EJ-232Q (% Benzophenone)				
		0.5	1.0	2.0	3.0	5.0
Light Output (% Anthracene)	55	19	11	5	4	3
Scintillation Efficiency (photons/1 MeV e^-)	8,400	2,900	1,700	770	610	460
Wavelength of Maximum Emission (nm)	370	370	370	370	370	370
Rise Time (ps)	350	110	105	100	100	100
Decay Time (ps)	1600	700	700	700	700	700
Pulse Width, FWHM (ps)	1300	360	290	260	240	220

the world of scintillating perovskites



effect of coumarin-6

⇒ strong blue-to-green WLS:

synthesis of $CsPbBr_3$

substitution of 50% of Br with Cl

addition of coumarin-6

for the primary (matrix + quantum dot) spectra to be peaked in blue ⇒ can shift to green

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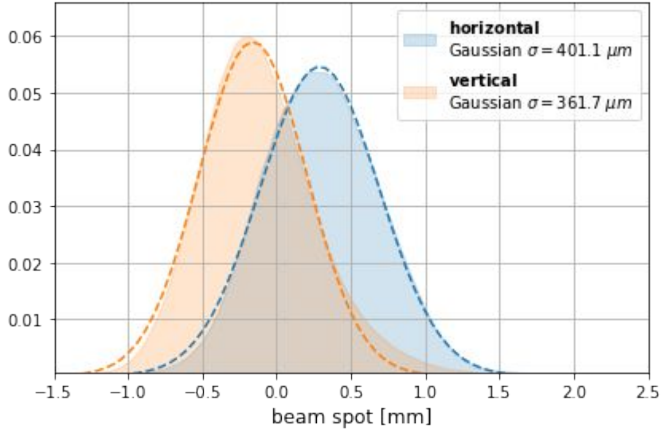
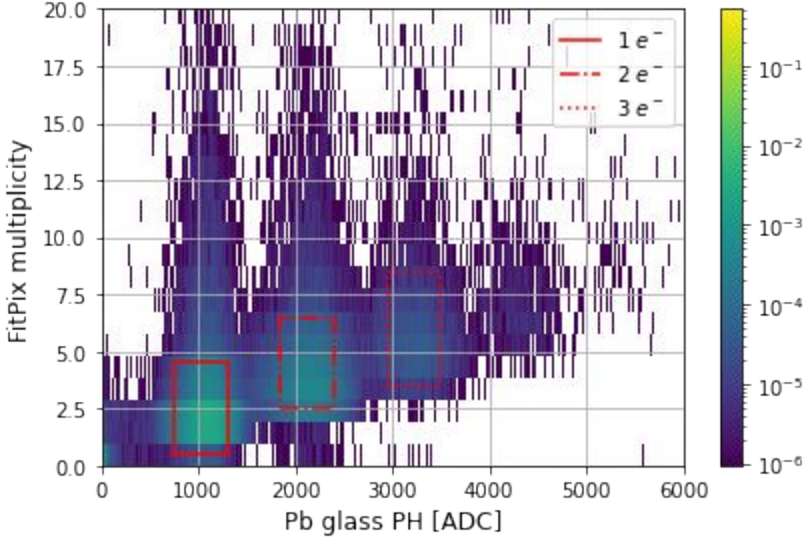
the beam





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the SiPM amplifier