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SUPPLEMENTARY INFORMATION

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Supplementary Information

Efficient, Fast and Reabsorption-free Perovskite Nanocrystal-based Sensitized Plastic Scintillators

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Supplementary discussion

The mechanism leading to the sensitized emission of **1** could be more complex using ionizing radiation than UV illumination, likely involving co-existing processes activated by primary interaction of the ionizing radiation in the NCs, as well as in the polymer matrix.

Specifically, primary interactions in the NC could produce, together with excitons, also high-energy free electrons, both by photoelectric effect and by Auger-mediated relaxation of deep holes, that could excite other NCs or **1** along their track. Monte Carlo simulations by Bulin *et al.*[28] have recently shown that a significant fraction of energy produced by primary interaction between ionizing radiation and NCs is indeed deposited outside the NC. In this case, the sensitization process is not solely determined by energy transfer from the NC excitons to the dyad and the dimming of the NC radioluminescence intensity with increasing [**1**] shown in Figure 2g,h could be caused also by a progressively larger fraction of propagating electrons being intercepted by **1** molecules. Similarly, excited NCs and **1** could be produced by electrons emitted by PMMA, however, this effect is likely very weak given the very large difference between the radioluminescence intensity of **1** in the presence and in the absence of the NCs.

Details of scintillation measurements using alpha particles

In these experiments, the same PMMA nanocomposites used for the radioluminescence experiments described before were faced to a 6×6 mm^2 Si photomultiplier (SiPM) composed of 14400 single pixels. When photons interact with this device, a number of cells proportional to the number of photons are activated, resulting in a current signal proportional to the number of activated cells. An operational amplifier converts this anode current into a voltage which enables us to evaluate the number of activated SiPM cells and thereby to quantify the number of detected photons. After performing calibration measurements described in the Methods section, the PMMA nanocomposites were faced towards the SiPM surface. To excite the light emission, we used two sources of ionizing radiation. The first is a ^{241}Am source that emits alpha particles with energy of 5.5 MeV. It also emits X-rays with energies ranging from 11 to 26 keV and γ-rays of 60 keV, but since the probability of interaction for alpha particles is much higher with respect to X- and γ-rays, the scintillation signals detected were ascribed to the alpha particles interacting with the nanocomposite. We also used ^{224}Ra and its radioactive daughters, that we implanted on the surface of the samples. The energies of the alphas emitted in the decay of such implanted nuclei range from 4 to 10 MeV. We measured a maximum light emission of 1000 ph per alpha event. Knowing that the alpha maximum energy was about 10MeV and that the total efficiency of light collection of our system is ~13%, a light emission of at least 1000 ph/MeV for alpha particles was evaluated.

Control experiments using $CsPbCl_3$ nanocrystals as non-resonant sensitizers

In order to discriminate between sensitization by nonradiative energy transfer from the effect of primary interactions between the NCs and the ionizing radiation, possibly leading to enhanced dyad (**1**) radioluminescence, we performed control experiments using $CsPbCl_3$ NCs as high-Z sensitizers. The rationale behind this choice is that, being the luminescence of $CsPbCl_3$ NCs not resonant with the main absorption of **1**, the sensitization by Förster energy transfer should be essentially negligible. Therefore, radioluminescence measurements on such blends vs. pure samples enables us to clarify the contribution by the increased interaction probability with ionizing radiation granted by NCs to the overall sensitization effect.

Extended Data Figure 1a shows the optical absorption and PL spectra of toluene solutions of the $CsPbCl_3$ NCs and of **1**. The NCs exhibit the typical sharp absorption peak at 390 nm and a narrow PL at 414 nm. Consistently, spectral overlap between the absorption spectrum of **1** and the PL peak of the perovskites is very small, resulting in negligible energy transfer from the NCs to **1.** This is confirmed by the identical PL decay dynamics of the $CsPbCl_3$ NCs embedded into PMMA nanocomposites (2.0%wt) in the absence and in the presence of **1** (0.155wt%), shown in Extended Data Figure 1b.

Based on these results, we proceeded with side-by-side radioluminescence measurements in the same excitation conditions and collection geometry of three nanocomposite samples, respectively embedding: **1** ([**1**]=0.155wt%), $CsPbCl_3$ NCs ([NCs]=2.0wt%) or their binary blend ([**1**]=0.155wt%, [NCs]=2.0wt%). The data are reported in Extended Data Figure 1c.

In stark contrast to the thirty-fold enhancement of the radioluminescence intensity of **1** by the $CsPbBr_3$ NCs reported in the paper, the addition of $CsPbCl_3$ NCs results in only a 6-fold intensification of the emission intensity, thus clearly highlighting the crucial and dominant role of Förster energy transfer in the sensitization process.

To further clarify this aspect, we use the data in Extended Data Figure 1c to estimate the various contributions to the sensitized radioluminescence of **1** through the expression:

$$I_{1,NCs} = I_1 + I_{1,NCs}^{Reabsorption} + I_{1,NCs}^{\chi}$$

Where:

- $I_{1,NCs}$, is the spectrally integrated radioluminescence intensity of **1** in the blended PMMA nanocomposite (that is, in the presence of the NCs).

-I_1, is the spectrally integrated radioluminescence intensity of **1** in PMMA in the absence of NCs.

- $I_{1,NCs}^{Reabsorption} = \mathrm{K} \cdot \Phi_{PL}^{1}$, is the portion of the spectrally integrated radioluminescence of **1** due to reabsorption of the NCs radioluminescence by the dyad. This value is extracted as the product of the PL quantum efficiency of the dyad (Φ_{PL}^{1}) and the term $\mathrm{K} = (1 - I_{NCs,1}/I_{NCs}^{0})$ extracted as the drop of the spectrally integrated radioluminescence intensity of the NCs in the blended nanocomposite ($I_{NCs,1}$) with respect to the nanocomposite embedding the NCs alone (I_{NCs}^{0}). We notice that this term already accounts for self-reabsorption by the NCs.

- $I_{1,NCs}^{\chi}$, is the contribution to the spectrally integrated radioluminescence of the dyad by electron transfer or other excitation processes (generically indicated with the letter χ).

Through this semiquantitative analysis, we obtain that χ-processes in the $CsPbCl_3$:**1** blend account for ~3.6-fold enhancement of the radioluminescence intensity of **1** (corresponding to ~60% of its total radioluminescence intensity measured), whereas a ~1.5 enhancement factor (corresponding to ~26% of the total dyad radioluminescence) is due to excitation of **1** by

reabsorption of the NCs radioluminescence. The remaining 14% is due to direct excitation of **1** by the X-rays.

Finally, we use these data to roughly estimate the contribution of energy transfer in $CsPbBr_3$:**1** nanocomposites, in the approximations that: *i*) $CsPbBr_3$ and $CsPbCl_3$ NCs have the same interaction probability with X-rays and, *ii*) reabsorption of the NCs radioluminescence by **1** is negligible in $CsPbBr_3$-based nanocomposites owing to the ≥95% efficient energy transfer demonstrated in Figure 2 of the paper.

Within these assumptions, the results on the $CsPbCl_3$:**1** blend in Extended Data Figure 1c suggest that χ-processes in the $CsPbBr_3$:**1** nanocomposite account for ~17% of sensitized radioluminescence of **1**, whereas 80% of the signal is due to sensitization by energy transfer. The remaining 3% is due to direct excitation of **1** by the X-rays.