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Composite Fast Scintillators based on High-*Z* Fluorescent Metal-Organic Frameworks Nanocrystals

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Abstract

Scintillators, materials that produce light pulses upon interaction with ionizing radiation, are widely employed in radiation detectors. In advanced medical imaging technologies, fast scintillators enabling a time resolution of tens of ps are required to achieve high-resolution imaging at the millimetre length scale. We demonstrate that composite materials based on fluorescent metal-organic framework (MOF) nanocrystals can work as fast scintillators. We present the first prototype scintillator fabricated by embedding MOF nanocrystals in a polymer. The MOF comprises zirconium oxo-hydroxy clusters, high-*Z* linking nodes interacting with the ionizing radiation, orderly arranged at nanometric distance from 9,10 diphenylanthracene ligand emitters. Their incorporation in the framework enables prompt sensitization of the ligand fluorescence, thus avoiding the typical issues deriving from the intimate mixing of complementary elements. This proof-of-concept prototype device shows an ultrafast scintillation rise time of ~50 ps, thus supporting the development of new scintillators based on engineered fluorescent MOFs nanocrystals.

The detection of ionizing radiation is an important topic owing to its significant scientific and real-life technological implications.[1, 2] Many detectors exploit a scintillation counter, which records the light pulses produced upon interaction of radiation with a luminescent material, i.e. the scintillator. An important example of their use is the time-of-flight based positron emission tomography (TOF-PET), a medical imaging technique used in oncology.[3] It uses a coincidence time resolution (CTR) method based on the detection of two back-to-back photons emitted by annihilation of a positron in the tissue at different times. This difference is proportional to their path length difference, and therefore contains information on the annihilation position.[4] This latter is blurred by a time measurement uncertainty, *time resolution*, which is assessed on ~ 200-300 ps in commercial devices resulting in spatial resolution of few centimeters.[5] Forefront research aims to achieve a 10 ps time resolution. This would enable a resolution at the millimetre scale without the instrumentation required to manage complex reconstruction algorithms, which increases the image acquisition time and the signal noise. The TOF-PET sensitivity would be improved by one order of magnitude and, potentially, cost-effective scanners for broad use would be fabricated owing to a simpler architecture.[4, 6-8]

The realization of new scintillators[9-11] will be decisive towards TOF-PET development, since the commonly employed bulk and nanostructured inorganic crystals[1], organic chromophores and plastics,[12] do not present the synthetic versatility required to have full control over the properties affecting the time resolution, such as the quantum efficiency and timing of the scintillator output.[13] This highlights the pioneering work by Allendorf,[14] who demonstrated the scintillation of fluorescent metal-organic frameworks (MOFs). MOFs are crystalline systems consisting of clusters linked by coordinating organic ligands.[15-17] Variation of ligands enables quite easy structural modifications and properties tailoring, thus obtaining MOFs dedicated to applications that span from gas sensing to bioimaging and photon managing.[18-20] MOF can therefore be made using scintillating dyes as ligands, interconnected by clusters containing high atomic number (Z) elements that enhances the interaction with the ionizing radiation and sensitize the ligands luminescence.[12,21-23] Importantly, the MOF architecture can preserve the properties of constituent fluorophores pivotal to obtain fast and sensitive detectors, thanks to the controlled framing of the active species that avoid detrimental interactions.[13] Compared with the other nanomaterials currently explored, MOFs present therefore a unique opportunity to create an alternative class of scintillators with an outstanding level of structural and composition control[24, 25] as demonstrated by Lan.[26] However, devices exploiting scintillating MOFs have not been devised yet with photonic properties for applicative purposes.

Here we show the first example of nanocomposite scintillators based on fluorescent MOF nanocrystals embedded in a polymer matrix. Composite systems have been recently proposed to surpass the limits of traditional scintillators, in particular for the timing performances. Since the use of nanosized emitters is pivotal to obtain homogeneous materials and to favour the scintillation activation enhancing the interaction between the matrix and the included nanopowder,[1,27] we tuned the synthesis to obtain nanometre-sized MOFs. The appropriate intermolecular distances between the heavy Zr-oxo-hydroxy clusters and the fluorophore linker dicarboxy-9,10-diphenylanthracene (DPA) enable the sensitization of the ligand emission also by energy transfer. The nanocomposites were realized with cost-effective processing of prototypal polymers endowed with distinct mechanical properties: an elastomer (polydimethylsiloxane, PDMS) and a thermoplastic polymer (polymethyl methacrylate, PMMA). Their scintillation shows ultrafast activation dynamics well below the 100 ps threshold, poorly affected by light scattering. The results obtained, and the growing interest in scintillating nanostructured systems,[2, 12, 28, 29] strongly support the development of composite scintillators based on fluorescent MOFs nanocrystals for high-resolution imaging and fast timing applications.

Results

Figure 1A and B display the molecular and crystalline structures of the MOF nanocrystals, respectively (Methods). Scintillating DPA has been employed as ligand owing to its high fluorescence quantum yield (0.96) and sharp absorption and emission spectra, thereby mitigating emission reabsorption.[30] Moreover, its absorption is resonant with the near-UV emission typical of wide-gap metal oxide such as the ZrO_2[31-32], thus enabling the sensitization of luminescence by energy transfer. A bulk scintillator can be fabricated by loading the nanocrystals in a transparent polymer matrix. Panels C is a digital picture of a composite device under X-ray irradiation and panel D illustrates the scintillation mechanism occurring in these systems. The recombination of the free charge cascade, generated by the interaction of the ionizing radiation with the composite constituents, sensitizes the creation of singlet molecular excitons on the ligands that produces fluorescence through radiative recombination.

Synthesis and photoluminescence properties of the zirconium-based MOF nanocrystals.

Fluorescent MOF nanocrystals have been synthetized by a modulated solvothermal process of Zr-ion oxy-hydroxy clusters and the DPA luminescent ligand (Zr-DPA, Fig.1A).[21, 33] Zirconium-based MOFs were chosen to take advantage of their excellent thermal and chemical stability crucial for devices. The synthesis was regulated by tuning the amount of the modulator (acetic acid) of the crystals size, which can be adjusted from few tens to hundreds of nanometres while retaining the octahedral morphology (Methods, Supplementary Figures S1-S14).[34] Figure 2A shows the absorption and fluorescence spectra of nanocrystals with average diameter of 58±16 nm (Fig. 2B) dispersed in benzene (refractive index n = 1.50 at 450 nm). The absorption profile matches the vibronic structure of isolated DPA molecules,[30, 35] thus indicating the absence of significant fractions of aggregated species.

Under 360 nm excitation, the MOFs exhibit a blue fluorescence peaking at 440 nm with a photoluminescence quantum yield ϕ_{pl} = 0.43±0.07 (Methods). At the emission maximum, the signal intensity decays as a multi-exponential function with characteristic lifetime of τ_{exp} = 3.3 ns (Fig. 2B, Supplementary Table 2). By correlating the time resolved data with ϕ_{pl}, we estimate the radiative lifetime as $\tau_{rad} = \tau_{exp}/\phi_{pl}$ = 7.7±1.1 ns. This value is comparable to the one observed in apolar solvents such as benzene with similar refractive indexes,[35,36] thus suggesting that the effective n sensed by emitters in the framework resembles the one of benzene.[37] The discrepancy between the ϕ_{pl} of nanocrystals and isolated DPA is ascribed to surface defects that partially quench the singlets diffusing in the framework.[39] Accordingly, larger nanocrystals show an increased ϕ_{pl} = 0.64±0.09 (Fig. S40, Supplementary Table 3). However, we chose to employ the smallest nanocrystals to avoid handling difficulties during the processing of devices.

In order to highlight the potential technological transfer of these materials, we chose two polymer matrices with similar density but distinct structural and mechanical properties, such as PMMA and PDMS, as hosts for the nanocrystals. The PMMA is a rigid, amorphous glassy polymer (T_g = 120°C, n = 1.50 at 450 nm), employed for its structural robustness and stability. Conversely, the elastomeric nature of PDMS (T_g < -122°C, n = 1.44 at 450 nm) at room temperature make it suitable for the realization of shaped objects.[38] (Methods, Figs. S28-S33). Two nanocomposites, low ($C_{low} =$ 0.05 weight % of MOF in the composite) and high ($C_{high} =$ 0.5 weight % of MOF in the composite) loading, were prepared for each polymer. Figures 2C-F depict the effect of the embedding of nanocrystals on their photoluminescence properties. Under 405 nm excitation, the C_{low} samples show a blue photoluminescence peaked at 450 nm and 464 nm for PMMA and PDMS, respectively, slightly red shifted with respect to the dispersion case due to partial emission reabsorption (Fig.4A). The photoluminescence intensity decays with characteristic lifetime τ = 5.3 ns in PMMA and 4.4 ns in PDMS. Considering their refraction indexes, no major change of the radiative decay rates of ligand excitons is expected. Thus, the increase of the photoluminescence lifetimes occurs thanks to the capability of the polymers to partially inhibit the non-radiative relaxation pathways constituted by MOF surface defects (Figs. S41 and S42) This increment suggests a growth of ϕ_{pl}, thus the nanocomposite external photoluminescence quantum yield ϕ_{pl}^{ext} was measured using an integrating sphere, as the ratio between the number of emitted photons exiting the sample over the absorbed ones (Methods). In agreement with the extended emission lifetimes, ϕ_{pl}^{ext} is assessed as high as 0.62±0.09 in PMMA and 0.51±0.07 in PDMS, thus demonstrating that the embedding is beneficial for the nanocrystal emission properties.[36] A direct evidence of close contact between the host polymer and the MOF surfaces is independently demonstrated by the efficient magnetization transfer across the heterogeneous interfaces, as shown by 2D ^{1}H-^{13}C NMR: however, at short contact times a larger interaction was observed in PMMA nanocomposite, in agreement with the larger increment of both photoluminescence lifetime and efficiency (Figs. S37 and S38). At high MOF concentration (C_{high}), both the samples display a greenish photoluminescence peaked at 485 nm. Beside re-absorption, we ascribe this effect to a less homogenous dispersion of nanocrystals that results in partial aggregation, as confirmed by transmission electronic microscopy (Fig. S39). The marked multi-exponential character of the emission intensity decay with time further advises the presence of emitting aggregates. Consequently, due to non-ideal passivation and possible aggregation quenching, the emission lifetime τ' is shortened to 4.0 ns in PMMA and 3.7 ns in PDMS. Nevertheless, their ϕ_{pl}^{ext} remains assessed to values around ~ 0.25 (Fig. S41, S42), thus fully enabling their function as fast scintillators.

Radioluminescence properties of MOF nanocrystals and nanocomposite scintillators.

Figure 3A shows the radioluminescence spectrum of the nanocrystals powder compared to bare DPA powder under steady-state excitation with X-rays (Methods). The sensitization effect of the heavy zirconium oxo-hydroxy clusters is evident. Despite their similar densities, 1.05 g cm^{-3} and 1.1 g cm^{-3} for the MOF and DPA respectively, the nanocrystals emission is one order of magnitude more intense. The data in Fig. 3B suggest a potential scintillation sensitization pathway in MOFs. Isolated zirconium oxo-hydroxy clusters prepared as reference material show a weak radioluminescence peaked at 400 nm (solid line), which is resonant with the DPA absorption (dashed line). Considering these complementary emission-absorption properties and the proximity between clusters and ligands (~12 Å, Fig.1B), it is plausible that both Förster and Dexter non-radiative energy transfer mechanisms occur with high rate~~s~~ and yield from an excited cluster to its coordinating dyes.[39] Therefore, we suppose that the sensitization of the nanocomposite scintillation is due to the synergistic action of two mechanisms. First, the enhanced interaction with ionizing radiation given by the presence of heavy elements in the nodes, which promotes the formation of free charges that can recombine on the dyes pillaring the MOF as in organic scintillators.[40] Second, the energy transfer from excited clusters, which can also work as free charges recombination centres, to the anchored ligands. Notably, considering the short intermolecular distances within the framework, this energy transfer can activate the DPA emissive state with ultrafast kinetics without affecting the global emission dynamics.[39]

Figures 3C and D show the radioluminescence spectra of the C_{high} nanocomposites, which show a greenish emission matching the photoluminescence profile, thus suggesting that photons are produced by radiative recombination of the MOFs ligand's singlets (see Fig. S43 for the C_{low} nanocomposites data). Radioluminescence measurements under continuous irradiation up to a few hundreds of Gy (insets) demonstrate the emission stability and the absence of long-time phosphorescence due to carrier recombination at delayed times.[1, 41, 42] A remarkable radiation hardness is observed. For a huge exposure dose of ~5.5 kGy, the nanocomposite exhibits a mere ~10% decrease of the radioluminescence intensity (Fig. S44), without the dramatic drop observed in similar systems.[43, 44] In order to point out the role of the peculiar arrangement of the Zr-oxide clusters and emitters in the MOF architecture, we performed control experiments vs. a DPA-doped polymer and vs. a composite scintillator made by embedding separately DPA and clusters. The data reported in Fig.3D highlight the pivotal role of the MOF supramolecular organization in setting the scintillation performance. Upon addition of isolated clusters, the DPA-doped polymer radioluminescence is enhanced by a factor 1.5, due to the presence of heavier elements that improves the interaction with X-rays. On the other hand, remarkably, the coupling of clusters and emitters in the MOF architecture enables a six-times increment of the emission intensity. This finding strongly supports the proposed sensitization mechanism, which exploits energy transfer from an excited cluster to the closely located DPAs molecules within the framework further sensitizing their promptly activated emission. Conversely, this pathway is not possible in the case where emitters and clusters are located far apart, i.e. in the control sample. The sensitization effect is therefore observed both in powders and in plastic matrix, but additional studies are required to model the complex kinetics involved in the process.

The nanocomposites have been tested under operative conditions by exposing the material to a γ radiation source such as radioactive ^{60}Co and other sources (Fig. S45). Figure 3E reports the pulse height spectrum recorded with a SiPM photodiode detector (Methods). No photoelectric peak is visible, due to the low density and inhomogeneity of the material.[28, 29] In order to give a general description of systems where the photoelectric peak is usually difficult to observe, we propose a simple approach to have a conservative but reliable estimation of the intrinsic scintillation yield ϕ_{scint} of the Zr-DPA:PDMS composite. We assume that the maximum number of active channels in the pulse height spectrum marks the maximum energy deposition produced by a Compton interaction. In our case, the absolute number of emitted photons n_{em} is related to the experimental emission intensity by $n_{exp} = \rho\beta\chi n_{em}$, where $\beta = 0.26$ is the the geometrical detection efficiency (Methods, Supplementary Table 4), χ = 0.30 is the quantum efficiency of the photo-detector at the measured wavelength and ρ = 0.78 is an empirical correction factor estimated using a certified plastic scintillator EJ-276^{TM} as reference. We chose a plastic reference because also in this case none photoelectric peak is detectable (Fig. S45), thus allowing an affordable comparison in the same experimental condition. The nanocomposite has an upper limit of n_{exp} = maximum number of active cells = 56 ±6% photons, thus n_{em} results in 920±90 photons.[45] By considering that the maximum energy deposited through the Compton by the most energetic ^{60}Co γ-ray is 1.12 MeV, the pessimistic lower limit of ϕ_{scint} is calculated as 821±82 ph MeV^{-1}, a value comparable and even higher than the one of other fast emitters currently studied.[9, 46, 47] A second independent relative measurement made with ^{22}Na and SiPM using an inorganic scintillator (BGO) as reference resulted a ϕ_{scint} = 1160±350 ph MeV^{-1}, thus confirming the previous value (Supplementary Information, Fig. S46).

Lighting properties and time response of nanocomposite scintillators.

The ϕ_{scint} is an important figure of merit for a scintillator. However, in general, part of the generated light is not collected by the photo-detector due to a poor out-coupling or significant reabsorption, thus limiting the overall sensitivity. These aspects must be carefully evaluated especially in presence of light scattering, as like as in MOFs nanocomposites, since both phenomena can affect the scintillator light output and its time response. We therefore developed a model that simulates the propagation of photons generated within the Zr-DPA:PDMS nanocomposite including the scattering of traveling photons and their re-absorption/re-emission mechanism. Specifically, the model reproduces a scintillation measurement where a photodetector is coupled by an index matching material to the nanocomposite (Methods). The latter is homogeneously irradiated from the opposite face (Fig. 4E). The scattering is simulated as an artificial constant absorption background α_S superimposed to the material absorption spectrum. In a scattering event, the photon is not absorbed, but rather its propagation direction is randomized. The parameter α_S has been varied from 0 cm^{-1} up to 10 cm^{-1}, where it dominates over the nanocrystals absorption α_{MOF} = 0.32 cm^{-1} at 370 nm. In our sample, α_S = 7.8 cm^{-1} at 495 nm (Fig. S47). Figure 4A shows the simulated emission spectrum at the detector side, as a function of α_S. A trivial reabsorption effect is evident, since even for α_S= 0 cm^{-1} the emitters density is sufficient to redshift the emission maximum with respect to isolated DPAs. Notably, no further spectral shift appears by increasing α_S, thanks to the narrow overlap between the ligands' absorption and emission profiles that limits reabsorption even for long-distance travelling scattered photons. The inset shows the relative integrated intensity of the light that reaches the detector. Again, this intensity is not affected significantly by scattering, being reduced by a mere 0.25 factor at the maximum α_s considered. Therefore, we can assume that the scattering has negligible consequences on the device lightning properties.

The proposed model enables also an analysis of utmost importance. Because of the random deviation of their propagation direction by scattering, emitted photons are temporarily trapped inside the material and therefore travel for longer distances before detection. This delayed detection induces a broadening of the scintillation pulse, according to the width of the length distribution of the deviated paths, which affects the final time resolution. Figure 4B reports the calculated cumulative distribution of the distances travelled by photons before being collected in our system. As in the scattering free condition, more than 50% of the emitted photons travel for approximately 1 cm. By considering the speed of light in PDMS, the resulting broadening of the scintillation pulse is Δt ~50 ps, comparable with literature.[48] This value is negligible if compared to emission decay times of a few nanoseconds typical of conjugated emitters. Moreover, less than 10% of the reabsorbed photons are re-emitted during the detection of the scintillation pulse (inset), leaving the average luminescence lifetime of the systems virtually unaffected. On the other hand, Δt cannot be neglected when considering the scintillation pulse rise time, which can occur in the sub-nanosecond time scale.[49] More precisely, both the scintillation rise (τ_{rise}) and decay (τ_{scint}) times must be evaluated, as they have a large impact on the achieved coincidence time resolution (CTR) expressed by

$$\mathrm{CTR} = 2.18\sqrt{\frac{\tau_{rise}\times\tau_{scint}}{N}}. \qquad \text{Eq.1}$$

Here the term $N = \beta\bar{\chi}\phi_{scint}$ is the number of detected photons at given irradiation energy[13] and the parameter $\bar{\chi}$ the photo-detection efficiency weighted over the emission wavelength of the scintillator, taken here as 0.5.[50] Equation 1 derives from mathematical arguments calculating the variance of the detection in time of the scintillation photons,[13] considering an ideal photodetector with instant answer, thus resulting the *ideal* CTR set only by the intrinsic scintillation properties of the material.

Preliminary experiments showed that the scintillation of both nanocomposites occurs in the nanosecond time scale, in agreement photoluminescence data (Fig. S48), thus demonstrating that no slow recombination dynamics are involved. With the aim to estimate the effect of scattering on τ_{rise}, we simulated the scintillation pulse by combining the time resolved photoluminescence data with the calculated time distribution of detected photons (Methods, Fig. S49). The scintillation light is assumed to be generated instantaneously as in common organic systems.[40, 49] The shape of the scintillation pulse in the sub-nanosecond time range is showed in Fig. 4C. The scattering-free system τ_{rise} is 54 ps, which considering a β = 0.38 and τ_{scint}= 3.7 ns results a CTR = 78 ps (Supplementary Table 4). Remarkably, for the high scattering case the τ_{rise} is only slightly slowed down = 60 ps. By combining this value with the corresponding β = 0.29, we obtain a theoretical CTR_s = 93 ps, in agreement with preliminary experiments indicating an activation mechanism much faster than 300 ps (Fig. S41). We also extended the modelling to different experimental configurations exploiting mirrors aimed to increase β (mid and right panel in Fig. 4C, Methods). However, the additional photons collected travel for longer distances due to scattering and thus are detected later. Consequently, the mirrorless case still shows the highest CTR_s value.

The simulation results are unambiguously confirmed by ultrafast time resolved scintillation experiments. Figures 4D, E show the scintillation pulse recorded by coupling the Zr-DPA:PDMS nanocomposite with a photodetector in the mirrorless configuration, upon excitation with ultrashort X-ray pulses (Methods). The plot shows that the scintillation pulse is build up with an excellent rise time τ_{rise} = 45 ps and decays with an average lifetime τ_{scint} = 4.1 ns (Supplementary Table 2), in agreement with the simulated and experimental data. All parameters in Eq. 1 are now experimentally determined, thus obtaining a CTR as low as 85±17 ps. This value is in excellent agreement with the model predictions, and, notably, it is comparable or even better than the one observed or calculated for other traditional and nanostructured materials.[9, 46, 47, 51, 52]

Discussion

The obtained results demonstrate that hybrid nanocomposite materials based on transparent polymers loaded with high-Z fluorescent MOF nanocrystals have the potential to be used as building blocks for making plausible alternative scintillating systems dedicated to fast detection of ionizing radiation. We show the sensitization of the MOF-ligand scintillation by the heavy elements incorporated in the framework architecture. Experimental evidence suggests that the scintillation is ascribed to the radiative recombination of molecular excitons on the nanocrystal fluorescent ligands, which are created by ultrafast recombination of photo-generated charges and possibly ultrafast energy transfer from the heavy linking nodes, thus preserving the recombination dynamics and yield of the fluorescence mechanism. The proof-of-concept prototype devices demonstrate an excellent radiation hardness and display an ultrafast scintillation activation dynamic, as well as a sufficiently high scintillation efficiency demonstrating a potential excellent timing performance that would enable detection with a time-resolution in the tens of picoseconds. This is of particular interest for advanced technologies employed for high-rate event detection and medical imaging applications. These systems can be realistically developed to be implemented in multicomponent detectors as the functional part dedicated to the timing. The analyses of devices' properties suggest indeed that there is a large room for improvements to meet the performance required in these demanding research fields. From a technological perspective, the modelling and experiments demonstrated that, for small size scintillators where no long-distance light propagation is required, the scattering produced by MOF nanocrystals neither significantly affect the lightening efficiency and the sensitivity of the detector, nor its sub-nanoseconds time-response. Moreover, the simulations show that the typical device engineering aimed to enhance its light-harvesting capacity does not significantly improve the system timing. Both these results are remarkable because they make fade, for small size devices, the constraints imposed by the synthesis of ultra-high optical quality materials and by the construction of complex architectures for enhanced light-harvesting, with beneficial effects on the processing, fabrication costs and implementation perspectives. From the fundamental point of view, the obtained data indicate that the key step to obtain the desired time resolution is to increase the scintillator light output. Several strategies can be pursued for this aim, since by engineering the MOF nanocrystals composition we can increase their density, scintillation yield, and radiative rate to boost their performance. For example, the incorporation of heavier elements such hafnium, in order to enhance the interaction with the ionizing radiation thus producing more photons, or the coupling with high-density materials in unconventional heterostructures.[10, 11] Also, the maximization of the system photoluminescence quantum yield through a better compatibilization of nanocrystals with the host polymer is forseeen,[36] as well as the use of self-absorption free multi-emitter MOF nanocrystals with large Stokes shift or the use of faster emitters. According to Eq. 1, all these approaches must be synergistically pursued in order to enhance the scintillation light output by the factor sixty required to lower the CTR close to the target value of ~10 ps. The presence of accessible pores is another important additional feature of MOFs that would allow for even better modulation of the material composition, for example by inclusion of elements and compounds aimed to implement selective interaction with different types of radiation. Lastly, by using advanced polymerization techniques and dedicated functionalization of MOF surfaces, it would be possible to fabricate highly loaded homogeneous bulk devices with specific mechanical properties according to technological requirements for the realization of cost-effective, compact and flexible fast detectors.

Figures Captions

Figure 1 | Composite plastic scintillator based on fluorescent metal-organic frameworks (MOFs) nanocrystals. **a,** Molecular structure of the MOFs building blocks. Zirconium oxo-hydroxy clusters frame fluorescent DPA ligands in a crystalline structure, which unit-cell is reported with a view along the *c*-axis. **b**, Sketch of the MOF tetrahedral and octahedral cavities. Yellow and green spheres diameters are 3 Å and 17 Å, respectively. **c**, Picture of the composite scintillator fabricated embedding MOF nanocrystals in a polymer matrix under X-rays excitation and **d**, outline of the photophysics involved in the scintillation process. Free charges are generated by interaction of the ionizing radiation with the polymer and MOF nanocrystals. They recombine generating emissive singlets on DPAs, which fluorescence can be detected by a photon counter. The resonance between the X-ray activated luminescence of clusters and the DPA absorption enable the sensitization of singlets by radiative and non-radiative energy transfer from excited clusters.

Figure 2 | Optical and photoluminescence (PL) properties of MOF nanocrystals and nanocomposites scintillators. a, b, Optical absorption, PL and time resolved PL spectra of MOF nanocrystals dispersed in benzene (6.5×10^{-10} M, optical path 0.1 cm). The inset of panel B shows the nanocrystals size distribution obtained by scanning electron microscopy (SEM) images analysis. **c-f**, PL and time resolved PL spectra of the two nanocomposites scintillators fabricated using PMMA (**c**, **d**) and PDMS (**e**, **f**) as host matrix. Two samples have been prepared for each polymer by embedding a C_{low}= 0.05% weight and C_{high}= 0.5% weight amount of nanocrystals, respectively. The solid lines are the fit of time resolved PL data with single exponential or multi-exponential decay functions. Insets are digital pictures of the nanocomposites under daylight and UV lamp excitation at 365 nm.

Figure 3 | Steady-state radioluminescence (RL) and scintillation of MOF-based nanocomposites. a, RL spectra of MOF nanocrystals, DPA and **b,** zirconium oxo-hydroxy clusters powders under X-ray exposure. Dashed line displays the DPA absorption. **c**, RL of PMMA polymer and Zr-DPA:PMMA nanocomposite loaded with C_{high}= 0.5% weight of MOF. **d**, RL of PDMS polymer and Zr-DPA:PDMS nanocomposite with C_{high} loading. The RL spectra of a polymer loaded with DPA (DPA:PDMS) and with separated DPA and clusters (DPA:clusters:PDMS) are shown for comparison. Insets of c,d: integrated RL intensity under continuous X-ray irradiation. The cumulated dose imparted is ~190 Gy (c) and ~135 Gy (d). **e**, Pulse height spectrum recorded by a SiPM photo-detector coupled to the nanocomposites exposed to a ^{60}Co γ-rays source (emitted photon energy 1173.2 keV and 1332.5 keV). **f**, Pictures of the Zr-DPA:PMDS nanocomposite exposed to X-rays and UV light.

Figure 4 | Scintillation properties of MOF-based nanocomposite. a, Normalized luminescence spectra calculated as function of the scattering level for the Zr-DPA:PDMS nanocomposite containing a C_{high}= 0.5% weight of MOF. Dashed line shows the emission spectrum of the isolated DPAs. The inset reports the integrated intensity of the output light. The red bar marks the nanocomposite scattering. **b,** Cumulative probability of the travel length distribution for scintillation photons in the device and (inset) of photon reabsorption events, as a function of the scattering level. **c**, Simulated scintillation pulses in three device configurations for scattering free (solid line) and highly scattering (α_s= 7.8 cm^{-1}, dashed line) samples. The reported coincidence time resolution (CTR) is calculated by Eq.1. **d, e**. Scintillation pulse decay (d) and rise (e) at 480 nm in the nanocomposite under pulsed x-ray excitation. The solid line is the fit of the pulse decay with a bi-exponential decay function.

Methods

Synthesis. MOF nanocrystals have been synthetized under solvothermal conditions. Briefly, $ZrCl_4$, dicarboxy-9,10-diphenylanthracene (DPA) and a suitable amount of acetic acid have been dispersed in a DMF/water mixture (see SI for further details). The resulting mixtures were heated at 120°C for 22 hours and the yellowish powders have been washed with fresh solvents and activated at 140°C under high vacuum. PMMA nanocomposites have been prepared through high temperature pressure molding of a dispersion of Zr-DPA nanocrystals in PMMA. The PMMA shows a prevailingly sindiotactic microstructure (dyads r = 70%). The nanocomposites were realized from the melt of the polymer/MOF mixtures at 200°C at which the fluidity is high enough to efficiently embed the MOF nanoparticles. The PDMS nanocomposites have been prepared by casting a dispersion of MOF nanocrystals in a proper mold where it has been cured at 60°C to obtain self-standing nanocomposites. The nanocomposites were obtained by the reaction of vinyl-terminated polydimethylsiloxane with polydimethylsiloxane-*co*-methylhydrosiloxane by curing at 60°C. The cross-linking starting from the polymer terminals ensures the flexibility of the chains and very low glass transition.[40]

Structure analysis and microscopy. MOF nanocrystals and nanocomposites structure and composition have been studied by means of powder x-ray diffraction (PXRD) structure refinement, nuclear magnetic resonance (NMR) spectroscopy, Fourier - transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), adsorption properties, helium picnometry, scanning electron microscopy ad, transmission electron microscopy (TEM). Details on the instrumental setup and on the measurements protocols employed are reported in the Supplementary Information file. The crystal structures were refined by the Rietveld method combined with molecular mechanics and plane-wave DFT calculations (see Supplementary Information).

Photoluminescence studies. Absorption spectra has been recorded with a Cary Lambda 900 spectrophotometer at normal incidence using quartz Suprasil cuvettes with 0.1 cm of optical path and an integrating sphere to eliminate scattering effects. Steady state photoluminescence (PL) spectra were acquired with a Variant Eclipse fluorimeter (bandwidth 1 nm) using quartz cuvettes with 0.1 cm of optical path. Time-resolved PL spectra of the nanocrystals dispersion have been recorded by monitoring the samples emission decay at 435 nm. The nanocrystals have been excited with a pulsed LED at 340 nm (3.65 eV, EP-LED 340 Edinburgh Instruments, pulse width 80 ps). The MOF nanocomposites were excited with a pulsed laser at 405 nm (3.06 eV, EPL-405 Edinburgh Instruments, pulse width 90 ps) to avoid direct excitation of the host polymer matrix. PL decay times are measured at the maximum of the emission spectrum. Relative and absolute PL quantum yield has been measured with different methods as described in the Supplementary Information file. Measurements were performed on cylindrical bulk specimens of diameter 1 cm and height 0.5 cm. The nanocomposites photoluminescence properties have been validated with two control samples for each composition (Supplementary Information).

Radioluminescence studies. Steady state RL measurements were carried out at room temperature using a homemade apparatus featuring, as a detection system, a charge coupled device (CCD) Jobin-Yvon Spectrum One 3000 coupled with a spectrograph Jobin-Yvon Triax 180 operating in the 200–1100 nm range. All spectra are corrected for the spectral response of the detection system. RL excitation was obtained by x-ray irradiation through a Be window, using a Philips 2274 x-ray tube with tungsten target operated at 20 kV. At this operating voltage, continuous x-rays spectrum is produced by a bremsstrahlung mechanism due to the impact of electrons generated through thermionic effect and accelerated onto a tungsten target. The dose rate is 9.97±0.35 mGy $mA^{-1}s^{-1}$ at 20 kV, and 17.91 ± 0.62 mGy $mA^{-1}s^{-1}$ at 32 kV, evaluated on quartz grain matrix. In order to record the sample PL in the irradiation chamber, the RL setup has been coupled to a 405 nm pulsed diode laser (EPL-405 Edinburgh Instruments) through an optical fiber allowing the illumination of the sample in the x-ray chamber. Dye and clusters concentrations in the control polymer samples loaded with DPA (DPA:PDMS) and with separated DPA and clusters (DPA:clusters:PDMS) are the same than in the nanocomposite.

Scintillation studies. Ultrafast scintillation experiments have been made using a Hamamatsu 9 keV X-ray source with ultrashort pulsed emission (FWHM 62 ps pulse width, and Instrumental response 130 ps). as excitation source, and a SiPM HPK S13360 3050 CS operated at 62 V bias voltage (10 V overvoltage, SPTR = 135 ps FWHM) as photodetector. For relative light yield measurements, with an EJ-276^{TM} plastic scintillator from Eljen Technologies^{TM} as reference. The natural ionizing radiation source used is a ^{60}Co source. This isotope beta decays with the subsequent emission of two gamma rays with energies of 1173.2 keV and 1332.5 keV. This source was placed close to the MOF based nanocomposites samples which were optically coupled to a 6×6 mm^2 Hamamatsu s13360-6050CS SiPM with an index matching grease and covered with the free edges with Teflon (reflectivity 99% at 450 nm). This results in an optical coupling factor β = 0.26 (Supplementary Table 4). The scintillation photons produced by the interaction of the gamma rays with the samples and read by the SiPM produce a signal with an amplitude proportional to the number of activated cells of the SiPM. The signals from the SiPM were collected with a 2 GHz, 12-Bit oscilloscope and analyzed to extract the pulse amplitude information. The proportionality factor between the number of activated channel and the output voltage of the acquisition chain was evaluated through a calibration measurement without samples. When no direct photon source illuminates the detector, single cells can be activated only by single electrons emitted by thermal effect. Consequently, amplitudes related to single, double and triple cell activation can be used to extract the voltage signal amplitude that corresponds to exactly 1 electron. The second relative method employed with a inorganic scintillator as reference is described in the Supplementary Information file.

Light propagation modelling. Simulations of the scintillator nanocomposite performances were carried out using a Monte Carlo ray-tracing method, in which the photon propagation follows geometrical optics laws and the interference is neglected because of the large nanocomposite dimensions in respect to the light coherence length. Each scintillation event generates randomly propagating photons whose fate is determined in a stochastic way. In particular, each photon can be absorbed (and eventually re-emitted) by a chromophore, isotropically scattered, and reflected or transmitted at the interfaces. When a mirror is placed on a nanocomposite surface, a fixed reflectivity = 95% has been considered independently to the polarization state and incidence angle of the light. In the case of bare interfaces, the Fresnel coefficients have been used to compute the reflection probability. The detector is supposed to be coupled to the nanocomposite with size 1.0×1.0×0.5 cm with an index matching medium, therefore the photon escape probability from this face is set to one. The scintillator contains the same amount of nanocrystals employed to fabricate the C_{high} specimens. All the specific events (absorption, scattering, transmission or reflection) are chosen according to random Monte Carlo drawing. All the simulations were performed using the experimental absorption/luminescence spectrum and emission efficiency (Φ_{PL}= 27%) of the chromophore. The nanocomposite scattering was supposed to give rise to a light attenuation corresponding to an absorption coefficient ranging from 0 to 10 cm^{-1}. Inside the material, for each ray, the inverse transform sampling method was applied to randomly generate the length of the optical path before absorption by the chromophores or scattering. Path lengths follow the exponential attenuation law determined by the wavelength-dependent absorption/scattering coefficient. A single-ray-tracing Monte Carlo simulation was repeated 10^5 times. When also the output-pulse time-evolution was computed, the number of repetitions was increased to 10^7 to achieve a proper statistical averaging and the output pulse shape was calculated by using the following assumptions: i) the photons generated by the scintillation event are uniformly distributed inside the scintillator nanocomposite; ii) the chromophores are promptly excited by the scintillation. Once a chromophore excited state is generated by scintillation of by reabsorption, the time required to emit a visible photon was determined using the rejection sampling applied to the accurate luminescence lifetime decay obtained from experiment. This time was then added to the time required to that photon for travelling its geometric path up to the detector with a velocity determined by the refraction index of the PDMS matrix, thus obtaining the corresponding detection mark. The mid and right panels in Fig. 4C report the simulated light pulse shapes calculated for a scintillator detector where a single mirror is deposited on the scintillator front face (mid) or where five mirrors (right) cover all the free surfaces, respectively. In the scattering-free case, the CTR is improved both in the one (β= 0.47) and in the five (β= 0.70) mirrors configuration, with maximum enhancement of 10%. In the high scattering case, where the β factor takes the value of respectively 0.35 and 0.61, the improvement of the geometrical coupling between of scintillator and is detector is frustrated by a deceleration of the pulse rise.

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Online content

Supplementary information are available online at …..

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Author contributions

J. P. and I.V. equally contributed to this work. J. P., A. P., and A.C. designed and synthesized MOF nanocrystals and fabricated the composites. J.P., S.B., P.E.S, C.B.X. and A.C. analyzed the nanocrystals and composites structural properties. I.V., R.C. and AV performed steady state radioluminescence studies. C.D., M.S, N.K, S.G and E.A performed scintillation experiments with pulsed x-ray sources, M.S, N.K, S.G and E.A light yield measurements. M.B. and L.G. performed scintillation measurements with natural radioactive sources. E.C.P., F.N. and A.M. performed and supervised photoluminescence studies. F.M. and A.M. developed the numerical modelling of nanocomposites optical properties. A.M. conceived and designed the project.

Competing financial interests

The authors declare no competing financial interests.

Additional information

Supplementary information is available in the online version of the paper. Correspondence and requests for materials should be addressed to A. M.