Quasi-thresholdless Photon Upconversion in Metal-Organic Framework Nanocrystals

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Keywords: photon upconversion - triplet-triplet annihilation - nanocomposite – nanocrystals – metal organic frameworks

Abstract.
Photon upconversion based on sensitized triplet-triplet annihilation (sTTA) is considered a promising strategy for the development of light-managing materials aimed to enhance the performance of solar devices by recovering unused low energy photons. Here, we demonstrate that, thanks to the fast diffusion of excitons, the creation of triplets pairs in metal-organic framework nanocrystals (nMOFs) with size smaller than the exciton diffusion length implies a 100% TTA yield regardless the illumination condition. This makes each nMOFs a thresholdless, single-unit annihilator. We develop a kinetic model for describing the upconversion dynamics in a nanocrystals ensemble, which allows defining the threshold excitation intensity $I_{th}^{box}$ required to reach the maximum conversion yield. For materials based on thresholdless annihilators, $I_{th}^{box}$ is determined by the statistical distribution of the excitation energy among nanocrystals. The model is validated by fabricating a nanocomposite material based on nMOFs, which shows efficient upconversion under few percent of solar irradiance matching the requirements of real life solar technologies. The statistical analysis reproduces the experimental findings, and represents a general tool for predicting the optimal compromise between dimensions and concentration of nMOFs with a given crystalline structure that minimize the irradiance at which the system starts to be fully operating.
In the last decade, the research on phenomena that involve the triplet state in organic systems, such as singlet-fission (SF)\textsuperscript{1,2} and thermally activated delayed fluorescence (TADF)\textsuperscript{3,4} received increased attention due to their potential application to solar cells and organic light emitting diodes technologies. Another important mechanism involving triplet states is the photon upconversion based on sensitized triplet-triplet annihilation (sTTA), which is considered a promising strategy for the development of light-managing materials aimed at enhancing the performance of solar devices by recovering unused low energy photons.\textsuperscript{5-10} As sketched in Fig. 1a, the sTTA upconversion relies on the annihilation of two optically dark triplets (TTA) of an emitter moiety, with energy below the device bandgap, which produces a high energy fluorescent singlet that emits a photon suitable to be absorbed.\textsuperscript{11-15} Dark triplets are sensitized through triplet-triplet Dexter energy transfer (ET) from a light-harvester, which implies that the sTTA upconversion is obtained in bi-component systems such as mixtures of the light-harvester/sensitizer and the annihilator/emitter moieties. Remarkably, in composition-optimized systems upconversion quantum efficiencies (QY\textsubscript{uc}) larger than 30\% can be achieved with excitation light intensities comparable to the solar irradiance, paving the way for real world applications of this photon managing technique.\textsuperscript{16}

It is worth pointing out that excited molecules in solution or molecular excitons in solids should collide in order to experience ET and TTA, because both of them occur via a short-range electron exchange mechanism.\textsuperscript{17,18} The triplets diffusion dynamic is therefore crucial to obtain high performance upconverting materials and devices.\textsuperscript{19,20} In particular, because of the bimolecular nature of TTA, the QY\textsubscript{uc} is not a constant as like for standard photoluminescence, but it depends on the excitation intensity $I_{\text{exc}}$. By setting the number of available excitons, it determines both the annihilation rate ($k_{TTA}$) and yield ($\phi_{TTA}$), i.e. the fraction of triplet deactivated by annihilation.\textsuperscript{21} It is easy to observe experimentally that at low intensities, when $k_{TTA}$ is negligible, the upconversion efficiency depends linearly on $I_{\text{exc}}$. Conversely, at high
A sensitiser with absorption coefficient $\alpha$ is excited into a singlet state ($S_1^*$) that efficiently undergoes intersystem crossing (ISC) into the triplet state ($T_1$). Energy transfer (ET) then competes with back energy transfer (back-ET) to emitter triplets. These triplets can either spontaneously decay (with rate constant $k_T$) or undergo triplet–triplet annihilation (TTA) to an excited fluorescent singlet state of the emitter. Dashed lines mark a radiation-less transition.

b) Sketch of the TTA mechanism upon pulsed excitation in a confined system, where triplets pairs are collected in non-interacting vessels of size $d$ shorter than their diffusion length $L_T$ forcing their annihilation (top panel), and in a classical bulk material, where the average distance between triplets pairs $R$ change with time (low panel).

Irradiances when the TTA becomes dominant, the $\phi_{TTA}$ approaches 100% and $QY_{uc}$ saturates to its maximum value $QY_{uc}^{max}$, being limited only by the statistical probability $f$ to form a singlet upon triplets annihilation, by the ET efficiency $\phi_{ET}$, and by the emitter fluorescence yield $QY_r$.\textsuperscript{21-23} For solar applications, it is therefore mandatory that the irradiance required for $QY_{uc}^{max}$, the so-called excitation intensity threshold $I_{th}$,\textsuperscript{21} is significantly lower than one sun to maximize the conversion efficiency regardless the illumination condition during daytime. In
order to fulfill this constraint, triplets should possess a large diffusion length $L_T$ that ensures high collisional probability even at low irradiances when their concentration is small. In other words, a fast diffusion environment is required to have $L_T$ larger than the average distance $R$ between two triplets, thus allowing their encounter and annihilation before spontaneous recombination to the ground state.\textsuperscript{24}

The fast diffusion requirement is fulfilled in metal-organic framework nanocrystals (nMOFs). A nMOF consists of an ordered network of emitter molecules interconnected by metal ions.\textsuperscript{25} These structures preserve both the properties of the constituent fluorophores, which do not interact with each other, and the high exciton mobility of crystalline molecular aggregates.\textsuperscript{26} The $s$TTA upconversion in nMOFs has been already proven but with limited efficiency because of the small QYs that characterizes these materials.\textsuperscript{27, 28} However, we recently demonstrated that the poor emission efficiency mainly arises from the presence of surface defects that act as quenchers. A proper surface passivation enables to obtain highly emissive nanocrystals,\textsuperscript{26} which then represent the ideal components for realizing upconverting materials based on TTA. The availability of nanosized upconverters is indeed pivotal for the realization of composite materials with tailored optical properties, which can be implemented in current technologies or that can represent new archetypes for more complex photonic systems.

The modelling of the $s$TTA upconversion in nanosized systems is therefore mandatory in order to point out the limiting factors of the material performance, and thus the guidelines for the design and synthesis of efficient upconverters at low powers. Specifically, we focus our attention on nMOFs with dimension $d$ of few tenths of nanometers where the condition $L_T >> d$ is always verified\textsuperscript{29-31} for triplet excitons (confined-TTA). It implies that each triplets pair created in a single nMOF annihilates before spontaneous recombination avoiding energy dissipation, thus achieving a $\phi_{TTA} = 100\%$. Therefore, each nMOF can be considered as an individual, thresholdless annihilator, under the only condition that at least two triplets are created in the same nanocrystal. Otherwise, upconversion is not allowed and isolated triplets
decay spontaneously. Notably, this peculiar annihilation dynamics can be evidenced by means of time resolved photoluminescence spectroscopy experiments. As sketched in the top panel of Fig.1b, under pulsed excitation the upconverted light is immediately generated in nanocrystals where at least two triplets are created, while no emission can be detected at longer times from nMOFs where a single triplet survives. This behavior is radically different from classical $s$TTA upconversion in bulk materials (classical-TTA), where an infinite volume is accessible to excitons. In this case, after the excitation pulse the intensity of the upconverted emission progressively decreases with the time until the density of triplets is reduced to the point that $Lr \ll R$, thus avoiding their encounter (low panel).\textsuperscript{32, 33}

Here, we analyze the $s$TTA upconversion in a nanocomposite based on a nMOF dispersion in poly(butyl-acrylate). The sensitization of the nanocrystal triplets occurs via ET from diffusing metallated porphyrins embedded in the host matrix. The confined–TTA process is described by a kinetic model that takes into account the statistical distribution of excitons in an ensemble of nanocrystals upon steady state photo-excitation. The model predicts a new kind of threshold excitation intensity ($I_{th}^{box}$) for thresholdless annihilators, which marks the excitation fluency required to fully activate the upconversion in the ensemble. The observed $I_{th}^{box}$ corresponds to an irradiance of $\sim$0.05 suns, highlighting once more the potential of $s$TTA upconversion for solar technologies. The threshold can be predicted by using few fundamental parameters characteristic of the nanocomposite measured independently, being therefore a powerful figure of merit for the design of next generation quasi-thresholdless upconverters for a large variety of photonic applications.

As sketched Fig. 2, photon upconversion is obtained in a nanocomposite made of fluorescent nMOFs embedded in a polyacrylate elastomeric matrix doped with sensitizers. The rubber matrix results in a bulk material suitable for applications, providing at the same time the passivation of nMOF surfaces required for high-performance upconversion. Each nMOF
behaves as a triplets collector, a sink for the energy harvested by the sensitzers that diffuse in the viscous host polymer and transfer this energy to nanocrystals upon collision. Figure 2a illustrates the building blocks employed to fabricate nMOFs. The organic ligand used is the fluorescent 4,4’-(anthracene-9,10-diyl)dibenzoate (ADB). The ADB units are bound to Zn$^{2+}$ ions thanks to the lateral phenyl rings, which are terminated with carboxylic groups thus enabling the growth of self-assembled frameworks. The employed microwave-assisted synthesis results in a white powder of nanocrystals with an average size of ~26 nm, as observed by transmission electron microscopy (TEM, Fig. 2b and Supplementary Fig. S1). The x-rays diffraction analysis (Fig. S2) indicates that the closest center-to-center distance between two ligands in nMOFs is ~0.9 nm, which is a distance that allows the triplets diffusion within the framework by homo-molecular Dexter energy transfer. The details of the nMOF synthesis and crystalline structure are reported in Methods section and in the Supplementary Information (SI) file. The top panel of Fig. 2c reports the photoluminescence and the photoluminescence excitation spectra of a nanocrystals dispersion in benzene. Upon UV excitation at 340 nm the nMOFs show a blue emission peaked at 440 nm with a fluorescence quantum yield $Q_Y^{fl} = 17\%$. By considering that the electronic properties of the ADB ligand are strictly similar to that of its precursor dye, namely the 9,10 di-phenylanthracene (DPA), we select the Pt(II)-octaethyl porphyrin (PtOEP) as light harvester, which is an effective sensitizer of DPA triplets. When excited in the lowest absorption band at 532 nm (Fig. 2c, low panel), the PtOEP undergoes fast intersystem crossing populating its phosphorescent triplet state. From here, when a sensitizer molecule hits the nanocrystals surfaces, the ET occurs to the triplet of the ADB molecules incorporated in the nMOF. Once verified the upconverting ability of nMOFs in benzene solution with PtOEP (Fig. S3), we fabricate the sTTA nanocomposite by mixing 3 mg of nMOFs with 1 ml of a butyl- acrylate/PtOEP solution (2×10$^{-4}$ M). Free radical polymerization of butyl- acrylate leads to the formation of polybutyl-acrylate, a rubbery polymer with glass transition temperature of about 220 K. In this case, the polymerization is conducted at room
Figure 2. a) Sketch of the nMOF composition and b) transmission electron microscopy (TEM) image of drop casted bare nMOFs. The inset shows the nanocrystals size distribution. c) Photoluminescence (PL), photoluminescence excitation (PLE) and absorption spectra of nMOFs and sensitizers PtOEP in benzene dispersion. The PtOEP molecular structure is reported as inset. d) Scheme of the synthesis route followed for the fabrication of the nanocomposite. e) Schematics of the sTTA upconversion mechanism in the material. Upon absorption of green photons, sensitizers diffuse in the polymer and subsequently transfer the absorbed energy by ET upon collision with the embedded MOF nanocrystals (nMOFs), which acts as triplet exciton collectors. Dark triplet excitons on the nMOF organic ligands, generated on the surfaces, diffuse within the crystal and undergoes TTA producing fluorescent blue emitting singlets.

Temperature for days (Fig. 2d) by the addition of the radical polymerization initiator 2,2’-azobis(isobutyronitrile) (AIBN, 0.1 mg). AIBN is one of the most used free radical initiators, it is thermally activated with a rate constant $k_d$ of $2.15 \times 10^{-7}$ (s$^{-1}$) at 313 K in CCl$_4$. Therefore, by performing the polymerization at room temperature the number of free radicals generated should be sufficiently low to ensure very high molecular weights, because furthermore combination and disproportionation reactions should be negligible. The material is prepared and sealed in a glove box under controlled nitrogen atmosphere. The selection of the poly butyl-acrylate (PBA) as host comes from previous studies on different upconverters. This rubber is obtainable under mild reaction conditions with good optical quality, and its local viscoelasticity does not prevent the molecular diffusion, which is mandatory for promoting the ET from sensitizers to nMOFs. Taking into account their structure, size and density, we estimate that the concentration of nanocrystals in the sample is $\sim 2 \times 10^{14}$ cm$^{-3}$ (3.2 $\times 10^{-7}$ M, see SI). This
is the highest concentration that enables to obtain a homogenous bulk material without any macroscopic aggregation of nanocrystals after the polymerization reaction (Fig. S6). On the other side, the loading of rubbers with nano-fillers is well known to potentially affect their mechanical properties. Especially relevant for our purpose it is the interaction between the nanocrystals surface and the polymeric host. In particular, polymer chains can be adsorbed on the surface and create an extended interphase of pronounced rigidity that can reduce the mobility of diffusing sensitizers and also potentially avoid a direct contact.\textsuperscript{41, 42} We performed therefore a series of mechanical and structural characterization experiments (Fig. S4) in order to monitor the material viscoelastic properties at the employed loading levels. The analyses demonstrate an intimate mixing of nMOFs with the soft host phase, without detrimental consequences on the diffusivity of PtOEPs.

We study the nanocomposite emission properties by means of steady state and time-resolved photoluminescence measurements. As showed in Fig. 3a, under excitation with a continuous wave (CW) doubled Nd:YAG laser at 532 nm, the material shows the peculiar photoluminescence spectrum of a sTTA upconversion system where, beside the residual emission of PtOEP due to an incomplete ET ($\Phi_{ET} = 0.60$, Fig. S5), we observe an anti-Stokes emission from nMOFs peaked at 440 nm. The inset shows that the blue emission is visible even with naked eyes through a short pass optical filter. The effects of the embedding on nanocrystals are analyzed by monitoring their fluorescence under pulsed excitation at 340 nm. Figure 3b compares the fluorescence decays of nMOFs dispersed in benzene and PBA with that one of the ABD ligand in PBA. In benzene, the time resolved PL spectrum of nMOFs behaves as a multi-exponential function with an average lifetime of 1.3 ns (see SI), which is about five times shorter than the one of ADB dispersed in PBA (6.1 ns). This decay dynamic is ascribed to a distribution of quenching centers that open additional non-radiative recombination pathways. This implies the drop of QY\textsubscript{f} from 85\% for ADB in benzene down to 17\% for the nMOFs
Figure 3. a) Photoluminescence (PL) spectrum of the nanocomposite under CW laser illumination at 532 nm (100 mW cm\(^{-2}\)). Inset: Digital pictures of the sample recorded without (left) and with a short pass blue optical filter (right). b) Time-resolved fluorescence spectrum at 435 nm of \(n\)MOFs dispersed in benzene and in poly butyl-acrylate (PBA), compared with the decay of the isolated ligand ADB in PBA dispersion, under pulsed excitation at 340 nm. Solid line are the fit with a multieponential decay function. c) Calculated and experimental energy transfer yield \(\Phi_{ET}\) from PtOEP to \(n\)MOFs as a function of the nanocrystals concentration \(C_{em}\). The theoretical \(\Phi_{ET}\) is calculated in the Perrin approximation using a sensitizer/emitter contact radius \(R_c\) of 1 nm (dashed line) and 19 nm (solid line). d) Time resolved PL spectrum of the nanocomposite at 645 nm (crosses) and 435 nm (dots), under modulated excitation at 532 nm (10 mW cm\(^{-2}\)). Inset: comparison of the PL decay at 645 nm between the nanocomposite and a PtOEP-doped PBA sample (PtOEP:PBA).

dispersion. This effect is mitigated by the embedding of nanocrystals in the polymer that partially passivates their surfaces thus reducing the number of quenching centers.\(^{26}\) Consequently, the average fluorescence lifetime rises to 2.10 ns in the nanocomposite, which corresponds to an increase of QY\(_{fl}\) up to ~30%, as confirmed by the 28\(\pm\)4% yield measured with an integrating sphere (Fig. S10). The multi-exponential character of the emission decay...
suggests also the absence of significant leaking of ligands from \( n \)MOFs due to the degradation of the crystalline structure, since isolated ADBs in PBA show different recombination dynamics.

Photoluminescence spectroscopy enables the analysis of the ET step, which requires a special care because it involves a small donor molecule, as the PtOEP, and a supramolecular system as a giant acceptor. The Dexter ET involved is a short-range interaction, which needs the physical collision between two moieties to occur. When small molecules are employed, the contact distance \( R_c \) between the donor and the acceptor is usually given by the sum of the molecular radii \( R_c = R_d + R_a \approx 1-2 \) nm.\(^{34,43}\) The nanocomposite offers a different scenario. Each \( n \)MOF contains many closely packed acceptors, and only those on the surface are involved in the ET when an excited sensitizer hits the nanocrystal. We describe therefore each \( n \)MOF as an ideal spherical acceptor of radius \( R_{aMOF} \). This means that \( R_c \) increases to a length of tenth of nanometres, thus an efficient transfer can be achieved by using relatively small densities of acceptors. Indeed, even if the nanocomposite contains a low amount of \( n \)MOFs that usually prevents the Dexter ET in viscous environments such as PBA, we observe a transfer yield larger than 50%.\(^{34,43}\) In order to test quantitatively our model, we compare the measured \( \Phi_{ET} \) as a function of the acceptor/emitter concentration \( C_{em} \) (Fig. S6) with the values predicted in the rapid diffusion limit for different interaction radii (Fig. S6 and Fig. 3c). In this condition, the transfer rate is proportional to \( C_{em} \) and it is calculated as \( k_{ET} = 4\pi D_{sens} C_{em} R_c \), where \( D_{sens} = 9.0\times10^{-7} \) cm\(^2\) s\(^{-1}\) is the sensitizer diffusivity in PBA.\(^{17,20,38}\) Due to their size, the diffusivity of nanocrystals is considered negligible. The expected transfer yield is calculated as \( \Phi_{ET}(C_{em}) = \frac{k_{ET}(C_{em})}{k_{ET}(C_{em}) + k_{sens}} \), where \( k_{sens} = (\tau_{sens})^{-1} \) is the spontaneous recombination rate of PtOEP in absence of acceptors.\(^{38}\) The dashed line in Fig. 3c shows the transfer yield calculated for \( R_c = 1 \) nm, which clearly underestimates the observed values (squares). Conversely, the experimental data can be fitted with the theoretical \( \Phi_{ET} \) function calculated for \( R_c = 19 \) nm (solid line). This length is intermediate between the radius of the inscribed and circumscribed sphere to a cube.
with edge of 26 nm, i.e. the nMOFs average dimension inferred from the TEM data analysis. The diffusion-assisted nature of the ET observed in the nanocomposite is further confirmed by a low temperature experiment. The cooling of the material to 77 K (Fig. S6) leads to the disappearance of the upconverted emission and to the appearance of a strong PtOEP phosphorescence, due to suppression of the ET in the frozen polymer where the sensitizers are blocked and cannot reach the acceptors. Therefore, these findings validate the proposed model for the diffusion-assisted Dexter-type interaction between a small molecule donor and a giant acceptor species.

The time resolved analysis of the sensitizer residual phosphorescence is consistent with the proposed picture and gives us further insights on the PtOEP/nMOFs interaction. By exciting the PtOEPs with a modulated CW laser at 532 nm, Fig. 3d shows that the luminescence at 645 nm decays as a single exponential function for about 300 µs, which corresponds to a signal decrease of more than 90%. This behavior confirms that the ET occurs in the rapid diffusion limit.\(^{43}\) The corresponding decay time \(\tau_{fast}\) is 35 µs (inset). Notably, the spectrum shows a secondary slow decay component, which accounts for 2% of the total phosphorescence intensity. The lifetime of this component is \(\tau_{slow} = 3.5\) ms, which is even longer than the PtOEP radiative decay time in PBA (\(\tau_{sens} = 107\) µs).\(^{44}\) While the fastest component reflects the transfer from PtOEPs to nanocrystals, this slow luminescence is ascribed to a back energy transfer (back-ET) from nMOFs to sensitizers. Because the nMOF triplet has a lifetime significantly longer than the PtOEP triplet, the re-population from nanocrystals results in an apparent extra-long living delayed phosphorescence, which mirrors the spontaneous lifetime of nanocrystals triplets.

Importantly, the presence of back-ET implies that the ET yield obtained from time resolved data, \(\Phi_{ET} = \left(1 - \frac{\tau_{fast}}{\tau_{sens}}\right) \cdot 0.70\) overestimates the net transfer yield measured in steady state conditions \(\Phi_{ET} = 0.60\) (Fig. S5).\(^{13,45}\) The occurrence of back-ET is not usually detected in molecular system based on PtOEP and polyacenes at the employed concentrations, which
suggests that it arises from the peculiar nature of our emitters for confined-TTA, as discussed in the next section.

The peculiar behaviour of sTTA upconversion in MOF-based nanocomposites it is studied by a side-by-side comparison with respect to a standard bi-component organic solution, i.e. a mixture of DPA (10^{-2} M) and PtOEP (10^{-4} M) in tetrahydrofuran. Fig. 4b shows the log-log plot of the photon upconversion efficiency of the nanocomposite (triangles) and of the reference (dots) measured as a function of the excitation intensity \( I_{\text{exc}} \) at 532 nm in steady state condition on oxygen free samples (see Methods). The reference shows the typical behaviour of bulk systems where triplet excitons are free to move in an infinite volume. Until saturation at high powers, the upconversion yield rises smoothly with the excitation intensity, due to the increment of the triplets population that boosts the annihilation rate \( k_{\text{TTA}} \) in respect to the spontaneous recombination \( k_T \). This behaviour is described by

\[
QY_{\text{uc}}(I_{\text{exc}}) = \frac{1}{2} f \cdot QY_\text{fl} \cdot \Phi_{\text{TTA}}(I_{\text{exc}}) = \frac{1}{2} f \cdot QY_\text{fl} \cdot \Phi_{\text{ET}} \left[ \frac{k_{\text{TTA}}(I_{\text{exc}})}{k_{\text{TTA}}(I_{\text{exc}})+k_T} \right],
\]

where \( f = 0.5, \ QY_\text{fl} = 0.96 \) and \( \Phi_{\text{ET}} = 1 \) for the considered solution (dashed line). The yield \( \Phi_{\text{TTA}} \) is the only power dependent parameter, calculated by considering the dyes diffusivities.\(^{21}\)

The nanocomposite behaves differently, with a sharper transition from the low efficiency regime to the saturation that derives from the different annihilation dynamic in a confined environment where \( L_T \gg d \). As sketched in Fig. 4b, when two excitons coexist in a nMOF they annihilates producing a fluorescent singlet, thus giving rise to a \textit{UC-bright} nanocrystal with \( \Phi_{\text{TTA}} = 1 \) that is a thresholdless annihilator. Conversely, if only one exciton is present, the nanocrystal remains \textit{UC-dark}. In this case, the triplet dissipates its energy by back-ET or spontaneous recombination. The overall performance of the nanocomposite must be described therefore by considering the statistical distribution of the exciton population in the nanocrystal ensemble as function of the excitation intensity, instead of in term of the power- and diffusion-dependent annihilation rates.
Figure 4. a) Sketch of the recombination dynamics of triplet excitons in UC-dark and UC-bright MOF nanocrystals. If the average number of triplets created in a single nanocrystal is \( \langle n \rangle \geq 2 \), TTA can occur with 100% yield and thus we have a UC-bright nMOFs. Conversely, if \( \langle n \rangle < 2 \), the nanocrystal is UC-dark, because the isolated triplet can only recombine spontaneously with a rate \( k_T \) or back transfer (back-ET) its energy to a sensitizer that hits the crystal surface.

b) Comparison of the upconversion quantum yield (QY\textsubscript{uc}) measured as a function of the excitation intensity \( I_{exc} \) for the sTTA-UC nanocomposite (triangles) and for a standard DPA/PtOEP (10\textsuperscript{-2} M:10\textsuperscript{-4} M) solution in tetrahydrofuran (dots). The conversion efficiency for the nanocomposite is reported also as a function of the average number of exciton per nanocrystal \( \langle n \rangle \) calculated for each \( I_{exc} \). Dashed and solid line are the theoretical QY\textsubscript{uc} predicted respectively for the classical reference solution (classical-TTA) and of the threshold less up-converting nanocrystals (confined-TTA), as described in the text.

c) Calculation of the threshold \( I_{th} \) as a function of the nMOFs density \( C_{em} \) and of the nanocrystal size \( d \). The pink plane indicated AM1.5 solar irradiance at 532 nm with a bandwidth of \( \Delta \lambda=25 \) nm. d) Plot of the \( I_{th}^\text{box} \) and energy transfer yield \( \Phi_{ET} \) as function of the nMOFs size \( d \) calculated for the \( C_{em} \) used in the nanocomposite. Dotted lines indicate the AM1.5 solar irradiance at 532 nm with different bandwidths. The orange dot marks the observed threshold for the nanocomposite used in our experiments.

In this case, the conversion yield is

\[
\text{QY}_{uc} = \frac{1}{2} f \frac{\text{QY_\#} \Phi_{ET} P_n}{2} (I_{exc}). \tag{2}
\]

where \( P_n \) is the cumulative probability to have at least \( n \) excitons in the same nMOF in absence of annihilation. This latter can be calculated by means of the Poisson distribution function.
\( P_{n \geq 2} \) quantifies the fraction of \textit{UC-bright} nanocrystals, i.e. the upconversion active population, and depends only on \( I_{\text{exc}} \), which determines the centre of the poissonian distribution of excitons per nanocrystal \( \langle n \rangle \). As showed in Fig. 4b, the model reproduces accurately the experimental data. The solid line is the plot of \( \text{QY}_{\text{uc}} \) vs. \( I_{\text{exc}} \) calculated by Eq. 2 using \( f = 0.5 \)\textsuperscript{13} and experimentally determined power independent quantities. Data in Fig. 4a show a \( \text{QY}_{\text{uc}}^{\text{max}} \) of \(~6\%\), in very good agreement with the maximum yield of \(~5\%\) predicted by Eq. 2 considering \( P_{n \geq 2} = 1 \) and the experimental \( \Phi_{\text{ET}} = 0.60 \) and \( \text{QY}_{\text{fl}} = 0.28 \) values.\textsuperscript{13} Notably, these latter efficiencies are the parameters that actually limit the overall upconversion performance, which can be raised up by improving the \( n\text{MOFs} \) surface passivation and employing different polymeric host in order to reach the theoretical maximum upconversion yield.

It is worth pointing out that the calculation of \( \langle n \rangle \) does require to know the ratio between the excitation rate and the recombination rate \( k_T \) of confined triplets (see SI). However, the instantaneous occurrence of TTA in UC-bright \( n\text{MOFs} \) prevents obtaining \( k_T \) from the long-time tail of standard time-resolved photoluminescence measurements (Fig. 1b).\textsuperscript{46} In order to bypass this problem, we set up a pump and probe experiment in which the sample is first excited with a strong light pulse and then is probed with additional weak and short pulses at different delays \( \Delta t \) (Fig. S7).\textsuperscript{47} The first pulse generates the upconverted emission, after which only triplets in UC-dark nanocrystals survives. The probe pulses, by generating few additional triplet, make bright few of the dark \( n\text{MOFs} \) without altering significantly the number of excitons. In such a way, by monitoring the upconverted emission intensity synchronized with the probe pulses, we follow the time evolution of the triplets population in UC-dark nanocrystals obtaining \( k_T = 286 \text{ Hz} \), a value similar to that one of anthracene-like emitters in organic solvents thank to the surface-defect passivation by the polymer.\textsuperscript{48} Notably, the observed triplet decay matches the slow component of the sensitizer residual phosphorescence (Fig. 3d), which confirms that this latter is due to back-ET from UC-dark \( n\text{MOFs} \).\textsuperscript{46}
The results obtained show that the key advantage of the nanocomposite is that it reaches the maximum upconversion efficiency at excitation intensity lower than the solution. We quantify this performance improvement by monitoring the turn on of the high-efficiency regime that is marked by $I_{th}$. In bulk-TTA, $I_{th}$ is defined as the excitation intensity at which $k_{TTA}$ equals $k_T$, but this definition is not more applicable for nMOFs, where annihilation is the only effective decay pathway for confined triplet pairs. However, according to Eq.1, $I_{th}$ corresponds also to the excitation condition at which the system shows a conversion yield of 50% of its maximum value. Likewise, we define the critical excitation intensity $I_{th}^{box}$ for confined-TTA as the irradiance at which $QY_{uc}(I_{th}^{box}) = 0.5QY_{uc}^{max}$. According to Eq. 2, this happens when $I_{th}^{box}$ gives $P_{n≥2} = 0.5$, i.e. when 50% of the nanocrystals in the ensemble contains at least two triplets. This condition is satisfied when is $\langle n \rangle = 1.7$. Consequently, taking into account the absorption coefficient $α$ [cm$^{-1}$], $ϕ_{ET}$, the nanocrystal concentration $C_{em}$ and the spontaneous decay rate of nMOF triplets, the analytical definition of the excitation threshold in confined-TTA systems results as (see SI)

$$I_{th}^{box} = \langle n \rangle P_{n≥2} \frac{k_T C_{em}}{α ϕ_{ET}} = 1.7 \frac{k_T C_{em}}{α ϕ_{ET}}.$$

Eq. 3

The predicted $I_{th}^{box}$ for our material is $\sim 2 \times 10^{-4}$ W cm$^{-2}$, which is in very good agreement with the experimental data and, remarkably, it is one order of magnitude lower than the threshold $I_{th}$ $\sim 1.6 \times 10^{-3}$ W cm$^{-2}$ of the reference solution. $I_{th}^{box}$ corresponds to an incident photon flux of $5.4 \times 10^{14}$ ph cm$^{-2}$ s$^{-1}$ at 532 nm, which is twenty times smaller than the AM1.5 solar irradiance in the low-energy absorption band of the PtOEP.$^{49}$ It follows that the nanocomposite reaches $QY_{uc}^{max}$ under few percent of the sun irradiance, thus overmatching the requirement of solar technologies.

Eq. 3 point out the factors that rule the upconversion efficiency and therefore it can be used to understand where there is room for improvements. First, $I_{th}^{box}$ depends linearly on the
spontaneous decay rate of the triplets, which is strongly affected by the presence of quenching centres. Therefore, improved synthesis protocols that produce defect-free nanocrystals will allow reducing the threshold by decreasing $k_T$. The same result can be obtained by extending the absorption bandwidth of the sensitizer to increase the fraction of harvested solar photons. In this case, the absorption coefficient $\alpha$ must be replaced with the bandwidth-integrated absorptance $\alpha' = \int \alpha(\lambda) d\lambda$. The last two parameters to discuss are the transfer yield $\Phi_{ET}$ and the nanocrystals concentration $C_{em}$, which are strictly related each other because the transfer rate is proportional to $C_{em}$. In particular, a reduction of $C_{em}$ would in principle lower the threshold by increasing $\langle n \rangle$. However, the same reduction will result in a decrease of $\Phi_{ET}$ that will affect the threshold in the opposite way. Therefore, a trade-off between these two effects must be found. Fig. 4c reports the calculated as function of the nMOFs size $d$ and the weight concentration $C_{em}'$ of embedded nanocrystals. The nanocrystals size ranges from one nm, i.e. the molecular case, to $10^4$ nm, while $C_{em}'$ is varied between 0.01% and 10%. The calculation demonstrates that the threshold decreases by increasing the amount of nanocrystals, which enhances the ET rate and efficiency. The minimum threshold, corresponding to the optimal trade-off between $\Phi_{ET}$ and $\langle n \rangle$, is found as low as 3×10$^{-6}$ W cm$^{-2}$ for a $C_{em}' = 10\%$ and nanocrystals of size $d = 200$ nm. Importantly, this threshold corresponds to $\sim 10^{-3}$ suns considering the sensitizer absorption at 532 nm with a bandwidth of $\Delta \lambda = 25$ nm. In our case, the maximum loading level that allows having and homogeneous samples is $C_{em}' = 0.33\%$. Fig. 4d shows the $I_{th}^{box}$ calculated as function of d for this concentration. The minimum value of 3×10$^{-4}$ W cm$^{-2}$ is predicted for $d = 32$ nm, very close to the size of the employed nanocrystals, which is equivalent to an irradiance of 0.06 suns. Interestingly, the corresponding $\Phi_{ET}$ is relatively low, about 25%. The transfer yield (dashed line) quickly saturates to 100% using smaller nanocrystals with $d < 10$ nm, because of the increased number of acceptors, but the simultaneous reduction of $\langle n \rangle$ pushes $I_{th}^{box}$ to super-solar values. Conversely, $\Phi_{ET}$ becomes the
factor limiting the system performances for $d > 70$ nm, because the number of nMOFs is so low that the ET is almost prevented.

This analysis highlights that tailoring the dimension of nanosized annihilators is of outmost importance for the realization of an efficient composite upconverter. However, it is also important to outline that Eq. 3 gives a subsolar threshold using nanocrystals with size between 20 nm and 60 nm (Fig. 4d). This is pivotal for the material development, because this finding mitigates a potential strict constraint that would require an extremely careful control of the synthesis route to achieve monodispersed sizes. This advantage will be further enhanced using nanocomposites with extended absorption bandwidths. Indeed, with a $\Delta \lambda = 100$ nm the threshold will be about few percent of one sun even using nanocrystals with sizes ranging from 10 to 300 nm. Therefore, exploiting this relaxed condition, more efforts can be focused on to the preparation of high quality and defect-free nanocrystals as improved annihilators/emitters. Importantly, the findings presented are related to the structural properties of nanocrystals. In particular, the density of the acceptor/emitter moiety in the framework plays a fundamental role. For example, using nMOF with ADB ligands packed in closer configuration would be more favorable to the creation of coupled triplet pairs, by enhancing both the ET and the exciton diffusivity. Another interesting approach has been recently explored by Rowe and co-workers, which obtained upconversion in MOF functionalized with surface-bound sensitizers. This configuration assure a 100% ET yield without any molecular diffusion, but the low conversion yields reported suggest that further studies are required to shed light on the role of the surface sensitizer in both back-ET and MOF fluorescence mechanisms. Moreover, for solar applications this design implies that the amount of light harvesters per MOF is limited by the functionalization reaction yield with consequences on the optical density of the bulk composite that must be evaluated.
In conclusion, we demonstrated that the confinement of triplet pairs in MOF nanocrystals with sizes of tenths of nanometers, i.e. smaller than the diffusion length of triplet excitons, makes the probability of spontaneous recombination negligible in respect to the bimolecular annihilation rate, thus achieving thresholdless upconverters with a triplet annihilation yield of 100%. Even if the corresponding nanocrystal ensemble shows a threshold excitation intensity for achieving the maximum conversion yield, which depends on the statistical distribution of the excitation energy among the upconverting units, $I_{th}^{box}$ is well below the solar irradiance. The performance of this system has been modelled and a simple expression for $I_{th}^{box}$ has been obtained. The proposed model has been validated by using multicomponent nanocomposites, which consists of a rubber polymer matrix doped with triplet sensitizer dyes and loaded with annihilating/emitting MOF nanocrystals. Our system, thanks to a proper surface-defect passivation and to the optimized sensitizer and MOF concentrations, shows a threshold of few percent of the solar irradiance, which is one order of magnitude lower than the best solution-based systems developed in the last decade. Therefore, while more efforts must be focused in the development of highly emissive MOF nanocrystals, this nanocomposites represent the first prototype of the next generation of low power photon upconverters potentially suitable for real world solar applications.
ASSOCIATED CONTENT

Supporting Information.

Experimental methods, additional data and figures that support the structural and optical characterization of the MOF nanocrystals and nanocomposites, together with the details on the time resolved photoluminescence spectroscopy measurements performed and the exciton distribution calculation.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

A.M. acknowledges support from Università degli Studi Milano-Bicocca (Grant No. 2016 ATESP0052) and the Cariplo Foundation (Grant No. 2016-0925).
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