Non-Poissonian photon statistics from macroscopic photon cutting materials

Mathijs de Jong¹, Andries Meijerink¹ & Freddy T. Rabouw¹

In optical materials energy is usually extracted only from the lowest excited state, resulting in fundamental energy-efficiency limits such as the Shockley–Queisser limit for single-junction solar cells. Photon-cutting materials provide a way around such limits by absorbing high-energy photons and ‘cutting’ them into multiple low-energy excitations that can subsequently be extracted. The occurrence of photon cutting or quantum cutting has been demonstrated in a variety of materials, including semiconductor quantum dots, lanthanides and organic dyes. Here we show that photon cutting results in bunched photon emission on the timescale of the excited-state lifetime, even when observing a macroscopic number of optical centres. Our theoretical derivation matches well with experimental data on NaLaF₄:Pr³⁺, a material that can cut deep-ultraviolet photons into two visible photons. This signature of photon cutting can be used to identify and characterize new photon-cutting materials unambiguously.
Optical materials are used to convert the energy of photons into other useful forms. Examples include photovoltaic materials converting light into electrical energy, phosphors transforming one colour of light into another and photocatalysts using photon energy to make or break chemical bonds. In most materials the conversion process generates no more than one quantum of output energy (for example, an energetic electron or a colour-converted photon) per one photon absorbed. The energy efficiency of such processes has a fundamental limit that is approximately inversely proportional to the energy of the incoming photon. This is, for example, a major factor determining the Shockley–Queisser efficiency limit for single-junction solar cells.

The process of photon cutting or quantum cutting can substantially improve the energy conversion efficiency for high-energy photons by ‘cutting’ them into multiple lower-energy excitations. This possibility was first hypothesized in 1957 (ref. 2) and has since been demonstrated experimentally in various materials, including semiconductor quantum dots (multi-exciton generation)\(^{(2)}\), organic dyes (singlet fission)\(^{(8-14)}\) and lanthanide ions\(^{(15-18)}\).

Most experiments for the characterization of photon-cutting materials rely on (time-resolved) photoluminescence or transient absorption measurements as a function of excitation wavelength\(^{(3,6)}\) or density of optical centres\(^{(12,16,17)}\). Usually, the proof that photons are ‘cut’ into multiple excitations is indirect, except in rare cases where the excitations can be extracted with very high efficiency\(^{(7,19)}\). This leads to ambiguities in the identification and characterizations of new photon-cutting materials. For example, the occurrence of multi-exciton generation in semiconductor quantum dots is usually concluded from fast decay components in transient absorption data\(^{(3,20-22)}\), but these can also originate from trapping of charge carriers or charging of the quantum dots\(^{(23)}\). Triplet states in dye molecules can be generated by the photon-cutting process of singlet fission\(^{(11,14)}\), but also by regular intersystem crossing\(^{(9)}\). Similarly, non-radiative energy transfer from a highly excited lanthanide ion can result in photon cutting through distribution of the energy over multiple excited centres\(^{(15,16)}\), but it is not trivial to distinguish this from processes generating only one excitation, while excess energy is lost as heat\(^{(24)}\). In view of this, it is not surprising that previous studies have sometimes reported contradictory conclusions on the occurrence or efficiency of photon cutting\(^{(20,21,24)}\).

Here we propose that direct proof of photon cutting in a material is possible by the observation of non-Poissonian photon emission statistics. Bunched emission has been reported from multi-exciton states in single CdSe quantum dots\(^{(25)}\). However, analysing photon cutting on a single optical centre is challenging at best and impossible for many photon cutters that rely on energy transfer between centres. We derive here that a photon-cutting material exhibits photon bunching even if it contains a macroscopic number of optical centres. Photon bunching should therefore be observable from any photon cutter where the excitations can be extracted as light\(^{(15,16,23,26,27)}\). We demonstrate this phenomenon experimentally on the photon-cutting phosphor NaLaF\(_4\) doped with Pr\(^{3+}\) (ref. 28).

**Results**

**Derivation of photon bunching from a photon-cutting material.** We start from the general energy level scheme of a photon cutter (Fig. 1a). A high-energy photon (purple) excites the system to a high excited state Y. This is followed by a cascade of transitions: first to an intermediate excited state X (blue) and then further to the ground state G (red). In both steps of the cascade, a photon is emitted. Figure 1b is an exemplary photon detection trace of a single

![Figure 1](https://example.com/figure1.png)

**Figure 1 | The detection of photon bunching from a macroscopic photon-cutting material.** (a) Photon cutting in a material with ground state G, first excited state X and second excited state Y. A high-energy photon (purple) excites the system to excited state Y, after which a cascade of two relaxations take place: from Y to X (blue) and from X to G (red). (b) Photon detection trace of a single ideal optical centre as in a, assuming ideal detectors. (c) Photon detection trace similar to b, but for an ensemble of optical centres. (d) Photon detection trace similar to c, but for a detection efficiency of 0.5. Because of imperfect detection some of the photons are missed. (e) Photon detection trace similar to d, but assuming a dark count rate equal to the signal strength. The dark-coloured photons are dark counts, which in an experiment would be indistinguishable from regular counts. (f) Photon detection trace as in e, but without spectral distinction between the photons of different colour. (g) Cross-correlation functions for an increasing number of optical centres \((N = 1, 10, 10^2, 10^3)\). The solid lines are the analytical function for the limit of a large ensemble, the data points the results of Monte Carlo simulations. (h) Cross-correlation function at different excitation intensities, which correspond to different values for the steady-state population of the intermediate state. The solid lines are the analytical solutions and the data points the results of Monte Carlo simulations. (i) Cross-correlation functions for the experimental scenarios sketched in c-f. The solid lines are the analytical functions, the data points the results of Monte Carlo simulations. In Supplementary Note 1 we derive the analytical correlation functions for non-ideal scenarios.
optical centre exhibiting such cascade emission. All photons from the first transition (blue) are followed by a photon from the second transition (red), with as average time interval the decay time $\tau_X$ of the intermediate state $X$. For a material with a large number $N$ of optical centres the emitted photons are also bunched in pairs, but now the pairs overlap in time (Fig. 1c). The statistics of bunched emission are different from the statistics of regular (that is, non-photon cutting) photoluminescence. The peculiar photon statistics of a photon cutting material can be described mathematically and investigated experimentally using the normalized photon-photon cross-correlation function.

$$g^{(2)}(\tau) = \frac{\langle I_1(t)I_2(t+\tau) \rangle}{\langle I_1(t) \rangle \langle I_2(t) \rangle},$$

where $I_1$ is the intensity of the first emission step in the cascade and $I_2$ is the intensity of the second step. The cross-correlation function describes how likely it is to detect a photon from the second transition at time $\tau$ after detection of a photon from the first transition. In the Methods section, we derive the cross-correlation function analytically for an experiment on a macroscopic photon cutter (as in Fig. 1c) in which the first photon (blue in Fig. 1a) and the second photon (red in Fig. 1a) are spectrally separated and directed to two independent detectors with negligible dark count rates:

$$g^{(2)}(\tau) = 1 + \frac{1}{N_X} e^{-k_{BG} \tau},$$

with $N_X$ the steady-state population and $k_{BG}$ the decay rate of the intermediate level $X$. Bunching is observed as an additional signal decaying with rate $k_{BG}$ on top of a constant unity background caused by Poissonian photons statistics.

In Fig. 1g, we plot the analytical correlation function (lines) for an ideal photon cutting material together with the correlation function from a Monte Carlo simulation (dots), for different numbers of optical centres ($N$) in the material. The excitation rate is set at $\Phi = 2k_{BG}/N$, which corresponds to a constant steady-state population of $N_X = 2$ in the limit of large $N$. The cross-correlation function shows an increased likelihood of detecting a (red) photon from the second transition after detection of a (blue) photon from the first transition for any number $N$ of optical centres. The analytical model (equation (2)) matches well with the Monte Carlo results for an ensemble of emitters with $N > 10$, including macroscopic materials containing a number of optical centres on the order of Avagadro’s constant (Fig. 1g, green and blue), clearly revealing the occurrence of photon-pair emission in the photon statistics. The analytical model is less accurate for a small $N$ (yellow and red), because the approximation of no ground-state depletion is justified only for large $N$ and low excitation rates. In agreement with equation (2), Fig. 1h shows that an increasing excitation rate $\Phi$ (and therefore increasing steady-state population $N_X$) results in a smaller bunching amplitude. At the same time a higher excitation rate $\Phi$ results in a higher photon count rate and therefore in decreased statistical noise on the correlation function. Interestingly, the bunching signal and the statistical noise both scale with $1/\Phi$, so that the excitation rate has no net effect on the signal-to-noise ratio in a photon-bunching experiment. See Supplementary Fig. 3 for an analysis of what this means for the fit uncertainties.

Figure 1c–f illustrate complications that may arise in real experiments on photon-cutting materials. Ideally, the collection and detection of photons would have unity efficiency (Fig. 1c), but in practice this efficiency is finite so that many photon emission events go unnoticed (Fig. 1d). Moreover, detectors have a finite dark count rate leading to random background counts (Fig. 1e). Finally, for many photon-cutting materials it is not possible to spectrally distinguish the two photons emitted in the cascade process (Fig. 1f). The correlation functions for increasing experimental complexity are plotted in Fig. 1i. A non-unity detection efficiency does not lower the bunching amplitude, but only lowers the count rates and therefore increases the noise on the data (compare blue and green). Detector dark counts lower the bunching amplitude (yellow), and should therefore be minimal. (In Supplementary Note 1 we investigate the effect of dark counts analytically.) The bunching amplitude decreases further if the two emitted photons cannot be separated spectrally (red). The bunching signal now becomes symmetric about $\tau = 0$, because the order of detector clicks is no longer sensitive to order of the emitted photons (Fig. 3d).

**Experimental demonstration of photon cutting in NaLaF$_4$:Pr$^{3+}$.** To experimentally test the occurrence of photon bunching in the emission from a macroscopic photon-cutting material, we measure the phosphor NaLaF$_4$ doped with 1% Pr$^{3+}$ (ref. 28). We use ~10 mg of the material, containing $N = 10^{17} - 10^{18}$ optical centres that in the experiment are excited more or less homogeneously. Figure 2a shows the mechanism of photon cutting in Pr$^{3+}$: ultra-violet light excites the ion to the $3P_0$ level (level $Y$ in Fig. 1a), after which a radiative transition to the $1I_6$ level, rapid non-radiative relaxation to the $3P_0$ level (level $X$ in Fig. 1a) and a radiative transition to one of the $3H_4$ levels (level $G$ in Fig. 1a) follow. In Supplementary Fig. 2 and Supplementary Note 2, we discuss how other types of photon cutters, such as quantum dots exhibiting multiple-exciton generation, can be mapped on the model of Fig. 1a.

Our experimental setup is sketched in Fig. 2b. The blue photons from the first radiative transition and the red–green photons from the second radiative transition are separated (Fig. 2c,d) with a dichroic filter and sent to two independent detectors. Cross-correlating the two detector signals yields Fig. 2e. We observe an increased likelihood of detecting a red-green photon after detection of a blue photon. The inset of Fig. 2e shows that temporal decay of the bunching signal in the cross-correlation function (green) matches the photoluminescence decay of the intermediate $3P_0$ level (red), in agreement with equation (2). This is a direct proof of photon cutting in NaLaF$_4$:Pr$^{3+}$, with the $3P_0$ level of Pr$^{3+}$ as the intermediate state.

**The magnitude of photon bunching.** In Fig. 3a–c we show how the bunching signal changes with excitation density $\Phi$. The amplitude of the bunching signal (Fig. 3a) is inversely proportional to the excitation density, while the decay time is constant at 18.4 $\mu$s (Fig. 3b). This decay time is in good agreement with the reported 18 $\mu$s$^{28}$ of the intermediate state $3P_0$ (\(=X\) in Fig. 1a). Meanwhile, the ratio of count rates on the two detectors is constant at 0.33 red photons per 1 blue photon, in good agreement with the reported value of 0.40 (ref. 28).

With the aim to investigate the effect of spectral separation, we have performed the experiment both with and without spectrally separating the two photons emitted in the cascade process. Spectral separation was achieved by using a dichroic mirror in the emission path (as in Fig. 2e), while the experiment without spectral separation used a 50/50 beamsplitter. In Fig. 3d we show the two resulting cross-correlation functions. The cross-correlation function with spectral separation (green) is similar to the result in Fig. 2e. The cross-correlation function of the experiment with the 50/50 beamsplitter (grey) shows symmetric bunching with a lower amplitude, in agreement with the simulations in Fig. 1i (red). We derive in Supplementary Note 1 that the ratio between the bunching amplitudes of the experiments with and without spectral separation is related to the radiative efficiencies of the two transitions in the photon-cutting material. Based on
This we can estimate that NaLaF₄:Pr³⁺ emits 0.35 red photons per 1 blue photon. This agrees well with the value of 0.40 reported by Herden et al.²⁸ and with the value of 0.33 obtained from the ratio of the count rates (Fig. 3c).

We have shown that the bunching amplitude equals 1/Nₓ, where Nₓ is the steady-state population in intermediate state X. Throughout this work, we used low excitation densities, so that Nₓ = 5–100 (Figs 2e and 3) in our bulk powder. Such excitation is strong enough that the photon count rate is reasonable (10¹⁻¹⁰⁴ s⁻¹), but weak enough for a significant bunching amplitude. In Fig. 3e,f we investigate how long a measurement using weak excitation (Nₓ = 5; total count rate 1,500 s⁻¹) must last to clearly observe bunching over the Poissonian background. Figure 3e shows correlation functions for experiments with different durations T. In Fig. 3f we plot the fitted bunching amplitude as a function of experiment duration, including the 2σ confidence intervals on the fitted bunching amplitudes.
confidence interval on the fit (blue) and the standard deviation of the noise (red). Already after 5 min, the bunching amplitude exceeds the noise by 2σ and after 15 min by 6σ, although photon bunching is not yet clear by visual inspection of the cross-correlation function (Fig. 3e). The time $T_c$ at which the bunching amplitude and noise level are equal (green arrow in Fig. 3f) can be used to calculate the detection efficiency $η$ if either the efficiency of the first or second radiative transition is known (see Supplementary Information equation (16)). Based on the efficiencies reported by Herden et al., we estimate that our detection efficiency is $η = 0.4\%$.

**Discussion**

Our work has demonstrated theoretically and experimentally that a photon-cutting material exhibits bunch emission, even if it contains a macroscopic number of optical centres. In fact, the magnitude of bunching does not depend on the total number of optical centres, but only on the steady-state population of centres in the excited state. We predict that similar photon statistics should be observable for many other photon-cutters recently reported. An interesting analogy exists with cutting materials. We envision that at each step of the cascade, it is possible to determine the absolute photon-cutting efficiency of materials. Our work has demonstrated theoretically and experimentally that photon cutting for materials where controversy exists can be subsequently decayed further to the ground state at a rate $k_{XG}$. The expectation value for the population of state X as a function of delay time $τ$ after the clock on detector 1 is

$$\langle N_X(t) \rangle = N_X + e^{-k_{XG}τ}.$$  

with $N_X = \Phi N_{kX}$, the steady-state population of state X. The decay of this one centre has a negligible effect on the excited-state populations $N_G$ and $N_Y = \Phi N_{kYG}$ in the rest of the material, because we consider a macroscopic number of optical centres $N \gg 1$. Realizing that the detector count rates $(I_1$ and $I_2$) are proportional to the excited-state populations, we can express the normalized cross-correlation of the signals on detectors 1 and 2 as:

$$g^{(2)}(τ) = \frac{I_1(τ) I_2(τ + τ)}{I_1(τ) I_2(τ)} = \frac{N_Y(N_X(τ))}{N_Y N_X} = 1 + \sum_{N_X} e^{-k_{XG}τ}$$

**Monte Carlo simulation.** We performed rejection-free kinetic Monte Carlo simulations of an ensemble of photon-cutting optical centres, each with an energy-level structure as in Fig. 1a. The simulation keeps track of the populations $N_G$, $N_X$ and $N_Y$ in the ground state G, the intermediate state X and the highest-energy excited state Y. Three processes can occur in the ensemble of optical centres: (1) absorption at rate $Φ N_X$, (2) decay of a centre in state Y at rate $k_{YG} N_Y$ and (3) decay of a centre in state X at rate $k_{XG} N_X$. A simulation step consists of (A) randomly selecting one of the processes (1–3) to occur, taking into account the relative probabilities, (B) drawing a residence time $Δt$ from an exponential distribution with average $(Φ N_X + k_{YG} N_Y + k_{XG} N_X)^{-1}$, (C) updating the simulation time $τ$ by $τ + Δt$, (D) storing the time $τ$ in case of photon emission and (E) updating the populations of the three states. In the simulation of experiments with spectral separation, photon emission events from states X and Y are stored in separate channels. In the simulation of experiments with finite detector efficiency, photon emission events are randomly excluded from the storage. Dark count events were added separately by drawing the intervals between events from an exponential distribution with average $D^{-1}$, where $D$ is the dark count rate.

**Data availability.** The data that support the findings of this study are available from the corresponding author upon reasonable request.

**References**

1. Shockley, W. & Queisser, H. J. Detailed balance limit of efficiency of a single-junction solar cell. J. Appl. Phys. 32, 510–519 (1961).
2. Dexter, D. L. Possibility of luminescent quantum yields greater than unity. J. Chem. Phys. 21, 836–841 (1953).
3. Schaller, R. D. & Klimov, V. I. High efficiency carrier multiplication in PbSe nanocrystals: implications for solar energy conversion. Phys. Rev. Lett. 92, 187401 (2004).
4. Schaller, R. D., Agranovich, V. M. & Klimov, V. I. High-efficiency carrier multiplication through direct photogeneration of multi-excitons via virtual single-exciton states. Nat. Phys. 1, 189–194 (2005).
5. Shabaev, A., Efros, A. L. & Nozik, A. J. Multiexciton generation by a single photon in nanocrystals. Nano Lett. 6, 2856–2863 (2006).
6. Timmerman, D., Valenta, J., Dohnalova, K., de Boer, W. D. A. M. & Gregorkiewicz, T. Step-like enhancement of luminescence quantum yield of silicon nanocrystals. Nanotechnol. 6, 710–713 (2011).

**Methods**

**Photon correlation.** We used a microcrystalline NaLaF$_3$:Pb$^{2+}$ : 1% powder provided by Jüstedt and colleagues. Approximately 10 mg of powder was glued as a thin layer of a few mm$^2$ to a non-luminescent background using SPI silver paint. The spectral output of a Micropack DH-2000 deuterium lamp filtered using an $λ$-cut of 450 nm bandpass filter illuminated the CsI(Tl) crystal. The luminescence decay curve of the $3P_0$ state was obtained by pulsed excitation with an Ekspla NT 342B laser at 446 nm and detection at 609 nm using a Triax 530 monochromator and Hamamatsu H7422-02 photomultiplier tube, coupled to a PicoQuant TimeHarp 260 photo counting module set at a discriminator level of $-100$ mV.

**Derivation of bunching strength.** We derive the cross-correlation function for photons emitted by a macroscopic photon-cutting material with $N$ optical centres. Each centre has the general energy-level structure as in Fig. 1a: a highly excited state $Y$ can decay to an intermediate excited state $X$ and then further to the ground state $G$. The two steps have total transition rates $k_{YG}$ and $k_{XG}$, respectively, and radiative efficiencies $η_{XG} = k_{XG}/k_{YG}$ and $η_{YG} = k_{YG}/k_{XG}$ with the superscript ‘$r$’ denoting the radiative part of the transition rate. A continuous-wave light source pumps the centres from state $G$ to state $Y$ at an excitation rate $Φ = elho$, with $h$ the plank constant and $o$ the photon energy. The two photons emitted in the cascade process are separated spectrally and sent to two detectors (1 and 2, respectively), each with zero dark count rate. This model describes our experiment on Pr$^{3+}$ well, as explained in Supplementary Note 1. There we also discuss situations where spectral separation of the two emitted photons is not possible (such as for multi-exciton generation in colloidal quantum dots) or where dark counts are not negligible.

A photon count on detector 1 signifies that one of the optical centres in the material just underwent the transition $Y \rightarrow X$. This particular centre is therefore in the intermediate excited state X directly after the detection event and can subsequently decay further to the ground state at a rate $k_{XG}$. The expectation value for the population of state X as a function of delay time $τ$ after the click on detector 1 is

$$\langle N_X(t) \rangle = N_X + e^{-k_{XG}τ},$$

with $N_X = \Phi N_{kX}$ the steady-state population of state X. The decay of this one centre has a negligible effect on the excited-state populations $N_G$ and $N_Y = \Phi N_{kYG}$ in the rest of the material, because we consider a macroscopic number of optical centres $N \gg 1$. Realizing that the detector count rates $(I_1$ and $I_2$) are proportional to the excited-state populations, we can express the normalized cross-correlation of the signals on detectors 1 and 2 as:

$$g^{(2)}(τ) = \frac{I_1(τ) I_2(τ + τ)}{I_1(τ) I_2(τ)} = \frac{N_Y(N_X(τ))}{N_Y N_X} = 1 + \sum_{N_X} e^{-k_{XG}τ}$$
7. Böhm, M. L. et al. Lead telluride quantum dot solar cells displaying external quantum efficiencies exceeding 120%. *Nano Lett.* **15**, 7987–7993 (2015).

8. Paci, I. et al. Singlet fission for dye-sensitized solar cells: can a suitable sensitizer be found? *J. Am. Chem. Soc.* **128**, 16546–16553 (2006).

9. Smith, M. B. &Michl, J. Singlet fission. *Chem. Rev.* **110**, 6891–6936 (2010).

10. Chan, W. et al. Observing the multie exciton state in singlet fission and ensuing ultrafast multielectron transfer. *Science* **334**, 1541–1546 (2011).

11. Burdett, J. J. & Bardeen, C. J. Quantum beats in crystalline tetracene delayed fluorescence due to triplet pair coherences produced by direct singlet fission. *J. Am. Chem. Soc.* **134**, 8597–8607 (2012).

12. Walker, B. J., Musser, A. J., Beljonne, D. & Friend, R. H. Singlet exciton fission in solution. *Nat. Chem.* **5**, 1019–1024 (2013).

13. Wilson, M. W. B., Rao, A., Ehrl er, B. & Friend, R. H. Singlet exciton fission in polycrystalline tetracene from photophysics toward devices. *Acc. Chem. Res.* **46**, 1330–1338 (2013).

14. Bakulin, A. A. et al. Real-time observation of multie excitonic states in ultrafast singlet fission using coherent 2D electronic spectroscopy. *Nat. Chem.* **8**, 16–23 (2016).

15. Wegh, R. T., Donker, H., Oskam, K. D. & Meijerink, A. Visible quantum cutting in LiGdF₄:Eu³⁺ through downconversion. *Science* **283**, 663–666 (1999).

16. Vergeer, P. et al. Quantum cutting by cooperative energy transfer in Yb,Y₁₋ₓPO₄: Tb³⁺. *Phys. Rev. B* **71**, 014119 (2005).

17. van der Ende, B. M., Aarts, L. & Meijerink, A. Near-infrared quantum cutting for photovoltaics. *Adv. Mater.* **21**, 3073–3077 (2009).

18. Zhao, Q. Y. & Hu, X. Recent progress in quantum cutting phosphors. *Prog. Mater. Sci.* **55**, 353–427 (2010).

19. Davis, N. J. L. K. et al. Multiple-exciton generation in lead selenide nanorod solar cells with external quantum efficiencies exceeding 120%. *Nat. Commun.* **6**, 8259 (2015).

20. Trinh, M. T. et al. In spite of recent doubts carrier multiplication does occur in PbSe nanocrystals. *Nano Lett.* **8**, 1713–1718 (2008).

21. Pipers, J. H. H. et al. Assessment of carrier-multiplication efficiency in bulk PbSe and PbS. *Nat. Phys.* **5**, 811–814 (2009).

22. Saeed, S. et al. Carrier multiplication in germanium nanocrystals. *Light Sci. Appl.* **4**, e251 (2015).

23. McGuire, J. A., Joo, J. I. N., Pietryga, J. M., Schaller, R. D. & Klimov, V. I. New aspects of carrier multiplication in semiconductor nanocrystals. *Acc. Chem. Res.* **41**, 1810–1819 (2008).

24. Yu, D. C. et al. Insights into the energy transfer mechanism in Ce³⁺:Yb³⁺ codoped YAG phosphors. *Phys. Rev. B* **90**, 165126 (2014).

25. Fisher, B., Caruge, J. M., Zehnder, D. & Bawendi, M. Room-temperature ordered photon emission from multie exciton states in single CdSe core-shell nanocrystals. *Phys. Rev. Lett.* **94**, 087403 (2005).

26. Tabacnich, M. et al. Resonant energy transfer of triplet excitons from pentacene to PbSe nanocrystals. *Nat. Mater.* **13**, 1033–1038 (2014).

27. Thompson, N. J. et al. Energy harvesting of non- emissive triplet excitons in tetracene by emissive PbS nanocrystals. *Nat. Mater.* **13**, 1039–1043 (2014).

28. Herden, B., Meijerink, A., Rabouw, F. T., Haase, M. & Jüstel, T. On the efficient luminescence of β-Na(La₂₋ₓPrₓ)F₄. *J. Lumin.* **146**, 302–306 (2014).

29. Sommerdijk, J. L., Bril, A. & de Jager, A. W. Two photon luminescence with ultraviolet excitation of trivalent praseodymium. *J. Lumin.* **8**, 341–343 (1974).

30. Pijper, W. W., DeLaca, J. A. & Ham, F. S. Cascade fluorescent decay in Pb³⁺-doped fluorides: achievement of a quantum yield greater than unity for emission of visible light. *J. Lumin.* **8**, 344–348 (1974).

31. Meuret, S. et al. Photon bunching in cathodoluminescence. *Phys. Rev. Lett.* **114**, 197401 (2015).

32. Meuret, S. et al. Lifetime measurements well below the optical diffraction limit. *ACS Photonics* **3**, 1157–1163 (2016).

Acknowledgements

We are grateful to Thomas Jüstel and co-workers for supplying us with the NaLaF₄:Pr³⁺ sample. The work was supported by the EU Marie Curie Initial Training Network LUMINET (316906) and by the Netherlands Center for Multiscale Catalytic Energy Conversion (MCCEC), an NWO Gravitation programme funded by the Ministry of Education, Culture and Science of the government of the Netherlands.

Author contributions

F.T.R. conceived the idea of the experiment. M.d.J. designed, performed and analysed the experiment. F.T.R. derived the analytical correlation functions. M.d.J. performed the Monte Carlo simulations. M.d.J., A.M. and F.T.R. discussed the results and wrote the manuscript.

Additional information

**Supplementary Information** accompanies this paper at http://www.nature.com/naturecommunications

**Competing interests:** The authors declare no competing financial interests.

**Reprints and permission** information is available online at http://npg.nature.com/reprintsandpermissions/

**How to cite this article:** de Jong, M. et al. Non-Poissonian photon statistics from macroscopic photon cutting materials. *Nat. Commun.* **8**, 15537 doi: 10.1038/ncomms15537 (2017).

**Publisher’s note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2017