Electronic Supporting Information for

Non-convergence of blinking timescale of twelve-faceted perovskite nanocrystals observed through an advanced fluorescence correlation spectroscopy study

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Experimental section

Chemicals used

Caesium carbonate (Cs_2CO_3, ~99%), phenacyl bromide ($C_6H_5COCH_2Br$, ~98%), oleylamine (OAm, technical grade, ~70%), 1-octadecene (ODE, technical grade, ~90%), oleic acid (OA, technical grade, ~90%), lead oxide (PbO, ~99%), toluene (~99.9 %) and hexane (~97%) were purchased from Sigma-Aldrich. All reagents were used as received, without further purification.

Synthesis of d-PNCs
Synthesis of d-PNCs involves the following two steps.
(i) **Preparation of caesium-oleate**
Cs_2CO_3 (~21.7 mg, 0.061 mmol), OA (~0.12 ml), and ODE (~1 ml) were mixed in a 50 ml two-neck round-bottom flask (RB). The reaction mixture was subjected to vacuum drying at approximately 120 °C for around 30 minutes; after that, the reaction mixture was transferred to a nitrogen environment at the same temperature.[1-3] The mixture was then kept at a high temperature for about 1 hour until all the solid Cs_2CO_3 had dissolved.

(ii) **Harvesting of d-PNCs**
In a 25 ml three-neck round-bottom flask (RB), 5 ml of pre-dried ODE, phenacyl bromide (~120 mg, 0.6 mmol), and PbO (~45 mg, 0.2 mmol) were mixed with ~1 ml of OAm and ~1 ml of OA.[1-3] The mixture was subjected to vacuum for approximately 45 minutes before being transferred to a nitrogen atmosphere at 130°C. This condition was maintained for several hours until all the solids dissolve. Subsequently, the temperature of the reaction mixture was raised to approximately 220°C and held for 1 hour, followed by the injection of ~0.5 ml of cesium-oleate prepared in the previous step.[1] The reaction mixture was annealed for about 20 minutes

before being cooled in an ice bath. The crude sample was then centrifuged at 8,000 rpm for approximately 10 minutes. The residue was dispersed in hexane, and the supernatant was discarded. For further purification, the sample was washed with a hexane-MeOAc mixture (4:1) and centrifuged at approximately 6000 rpm. The residue was then dispersed in hexane for further optical studies.[2-5]

For the synthesis of cube- and rhombicuboctahedron-shaped PNCs, we employed a similar method to the one described above, with the exception of the annealing time after hot injection, which primarily determines the resulting morphology. Detailed information on the synthesis of PNCs with different morphologies can be found elsewhere.[3]

Our synthesized PNCs exhibit high photostability, as evidenced by their lack of photodegradation in a single-particle blinking study conducted at high power (Fig. S10).

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Instrument used

Absorption and emission spectra

Absorption spectra were recorded with a Jasco V-730 spectrophotometer, while steady-state PL spectra were obtained using an Edinburgh FS5 spectrofluorometer.

### Transmission electron microscope (TEM)

High-resolution TEM (HRTEM) images were obtained using a JEOL JEM-2100 electron microscope operating at 200 kV.

Powder X-ray diffraction (P-XRD)

The X-ray diffraction pattern of the sample was measured using a Bruker Davinci D8 Advance diffractometer with CuKα radiation (λ = 1.5418 Å).

Confocal microscope

FCS, sFCS, confocal imaging, PL-intensity trajectory, and anti-bunching measurements were conducted using a commercially available confocal microscope purchased from PicoQuant (Model MT 200).
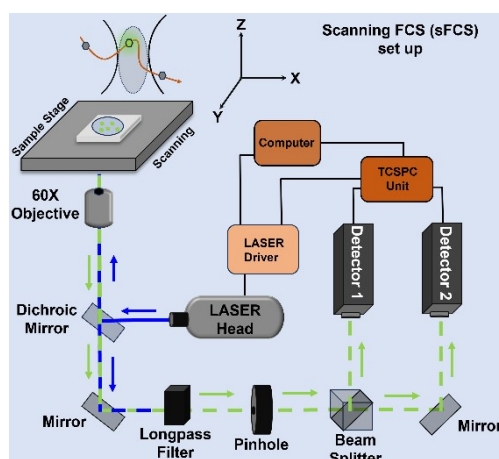
Scheme 1. Schematic of confocal microscope used for our studies

A specialized homemade sample chamber (shown below) was utilized for FCS studies to prevent sample spreading on the coverslip during recording
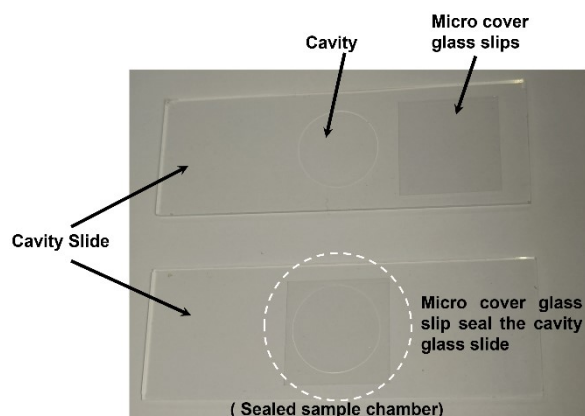
This chamber consists of a cavity slide filled with nanocrystal solution, covered with a coverslip. After sealing, the sample chamber is flipped and placed over the microscope objective (60x water immersion objective) for FCS measurements. A 422 nm pulsed diode laser was used for excitation, and a suitable long-pass filter was installed in the emission path to block the laser from reaching the detectors. A 50/50 mirror split the PL signal and directed it to two single-photon sensitive detectors (SPADs). A pinhole (~50 μm) was positioned in the emission path to remove out-of-plane signals. All analyses were performed using SymPhoTime 64 software developed by PicoQuant.

For anti-bunching, confocal imaging, PL-intensity trajectory, and sFCS measurements, a very dilute nanocrystal solution (dispersed in toluene with 1% PMMA) was spin-coated on a coverslip. This resulted in surface-immobilized nanocrystals where individual nanocrystals are embedded in the polymer matrix and separated by distances larger than the spatial resolution of a confocal microscope. A 100x oil immersion objective was used for the anti-bunching, PL-intensity trajectory, and confocal imaging studies. Scanning speed in sFCS was controlled using the SymPhoTime operating software provided with the setup.
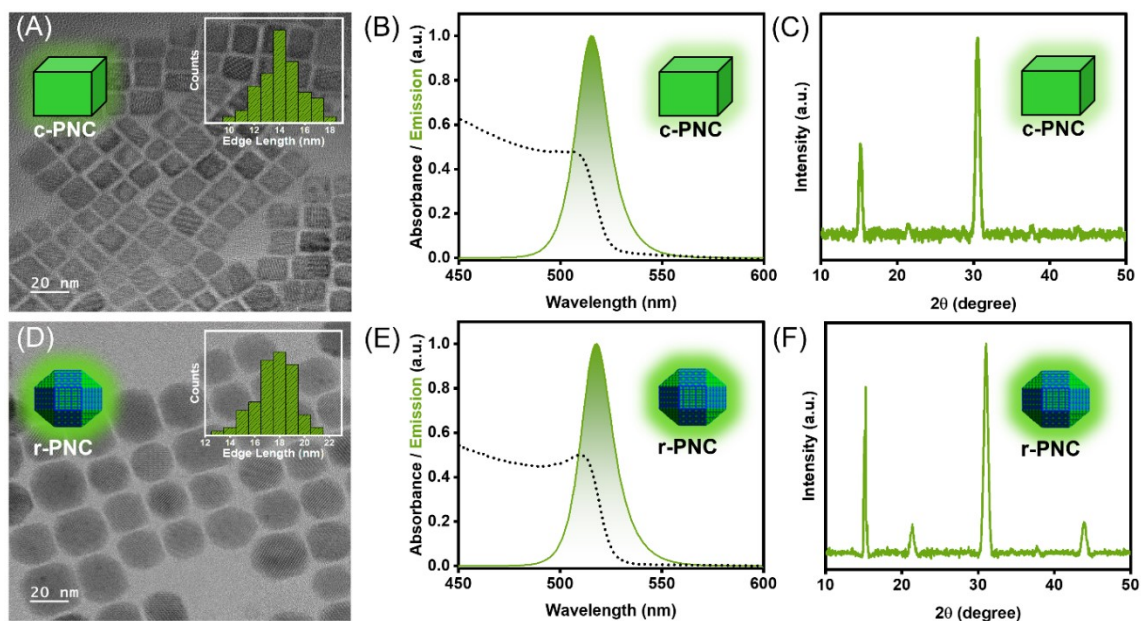
Fig. S1 (A, D) TEM micrographs of the cube (c-PNC) and rhombicuboctahedron (r-PNC) CsPbBr$_3$ PNCs along with the statistical distribution of particle sizes (inset). (B, E) Steady-state PL (green line, λ_{ex} ~400 nm) and absorption (black dotted line) spectra of cube and rhombicuboctahedron CsPbBr$_3$ PNCs dispersed in hexane. (C, F) Powder XRD spectra of cube and rhombicuboctahedron CsPbBr$_3$ PNCs. 3-D cartoons of particle morphologies are reproduced from ref 14. Copyright 2022 American Chemical Society.
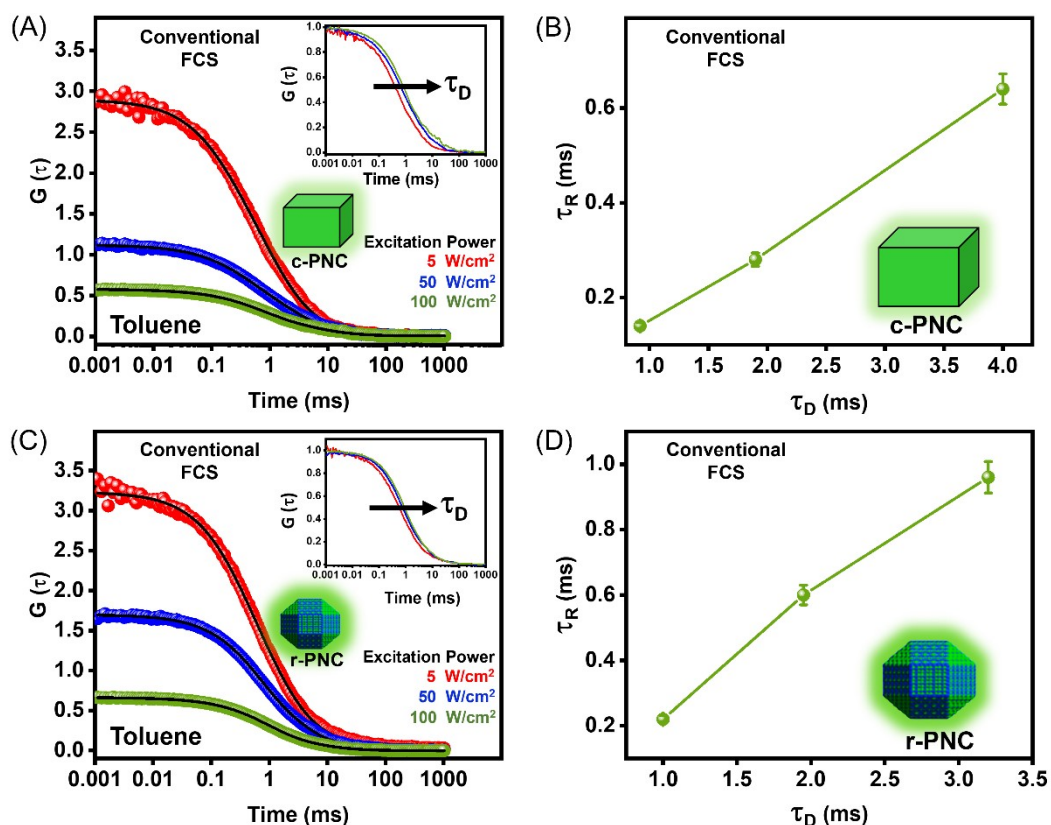
Fig. S2 (A, C) Conventional FCS curves (λ_{ex} ~422 nm) of cube-PNCs (A) and rhombicuboctahedron-PNCs (C) dispersed in toluene at different excitation powers. Individual curves fit nicely to Equation 2. The inset shows the same curves normalized at the initial time, showing τ_D slows down with pump intensity. (B, D) Plots of blinking timescale (τ_R) as a function of τ_D in toluene for cube-PNCs (B) and rhombicuboctahedron-PNCs (D), showing τ_R, without being converged, increases with increasing τ_D.
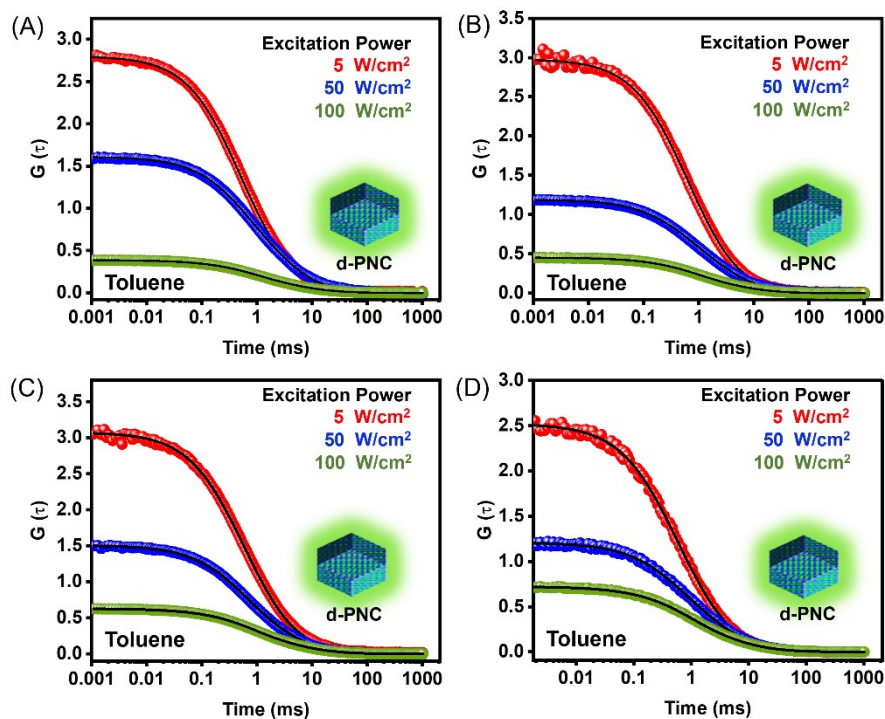
Fig. S3A Few representatives of repetition data from the experiment shown in Fig. 3A, with all experimental parameters maintained the same as in Fig. 3A.
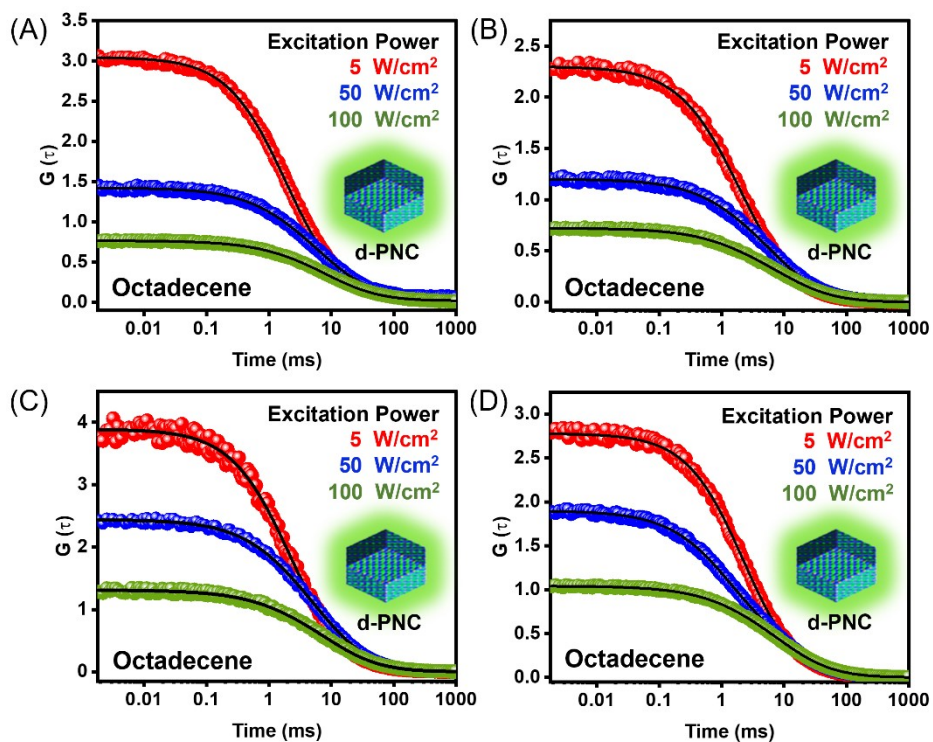

Fig. S3B Few representatives of repetition data from the experiment shown in Fig. 3B, with all experimental parameters maintained the same as in Fig. 3B.
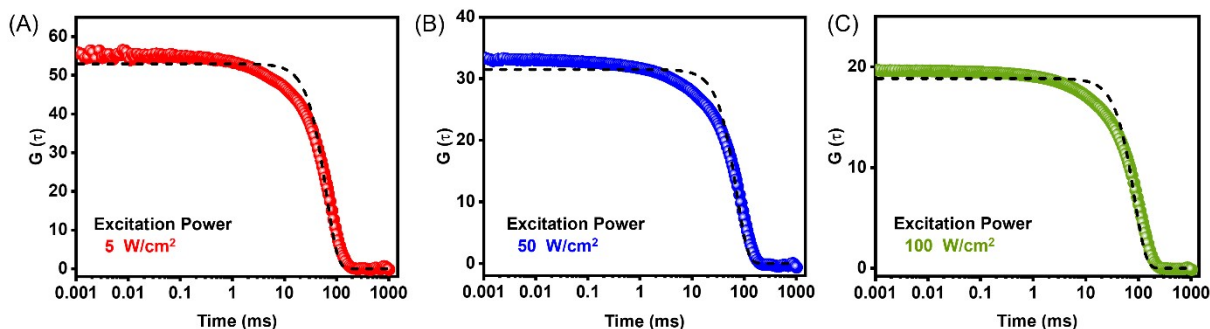
Fig. S4 sFCS curves (λex ~422) were recorded by scanning the surface-immobilized d-PNCs at various excitation powers. The fitted lines (black dotted lines), representing fits to the sFCS curves considering only with the scanning contribution $G_S(\tau) = [(1/N)\exp[-(\tau/\tau_s)^2]]$, were found to be unsatisfactory. This observation confirms the presence of blinking kinetics in the initial time regime of the sFCS curves.
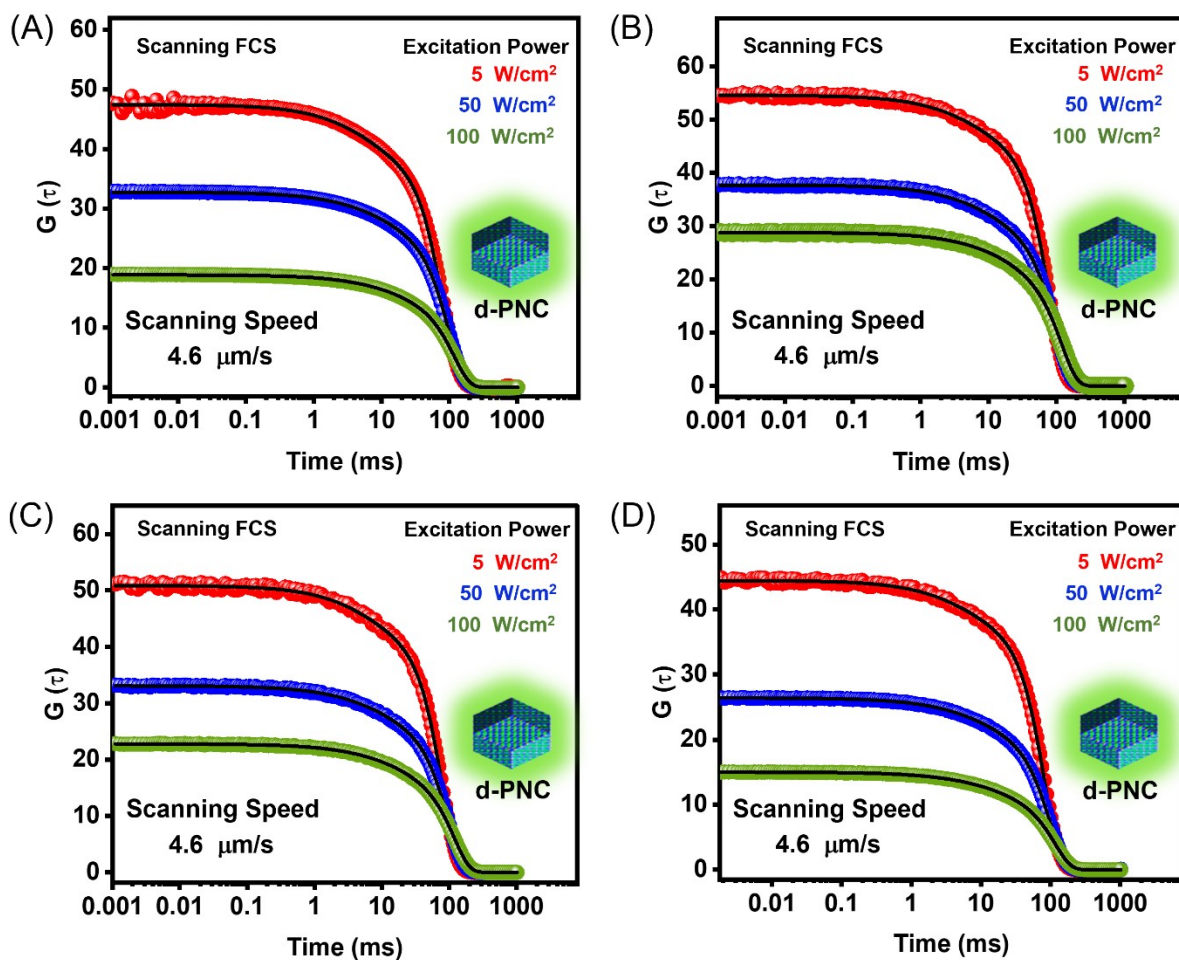

Fig. S5 Few representatives of repetition data from the experiment shown in Fig. 4, with all experimental parameters maintained the same as in Fig. 4.
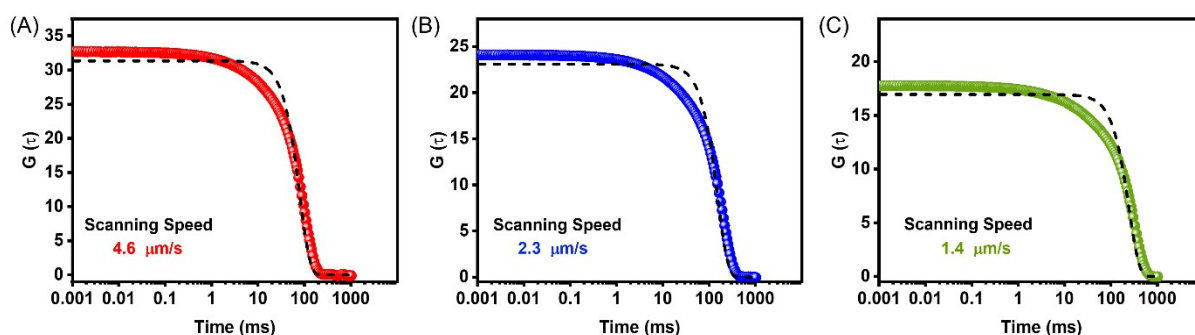
Fig. S6 sFCS curves (λ_{ex} ~422) were recorded by scanning the surface-immobilized d-PNCs with different speeds and at fixed excitation power (~60 W/cm^2). The fitted lines (black dotted lines), representing fits to these sFCS curves considering only the scanning contribution $G_S(\tau) = [(1/N)exp[-(\tau/\tau_s)^2]$, were found to be unsatisfactory. This observation confirms the presence of blinking kinetics in the initial time regime of the sFCS curves.
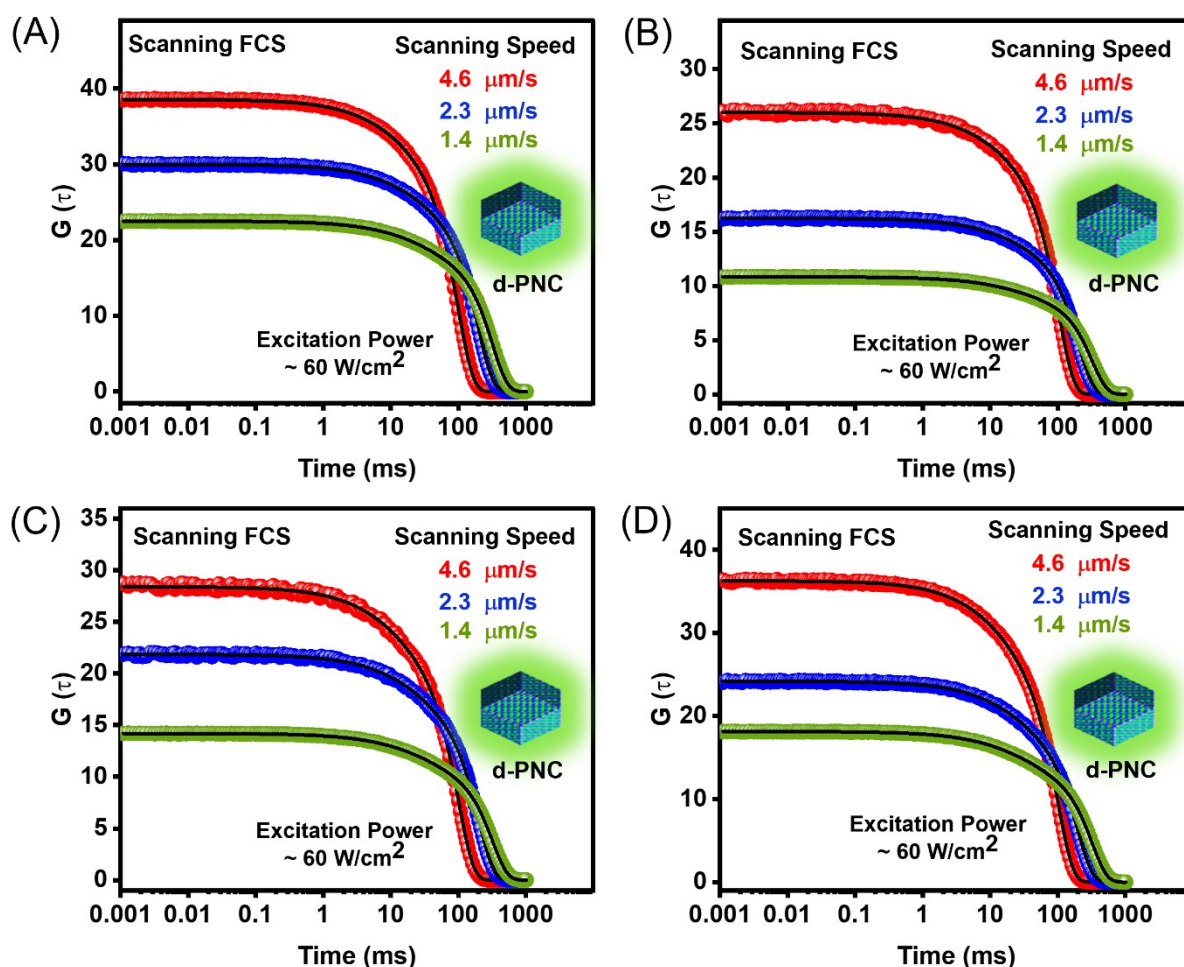

Fig. S7 Few representatives of repetition data from the experiment shown in Fig. 5, with all experimental parameters maintained the same as in Fig. 5.
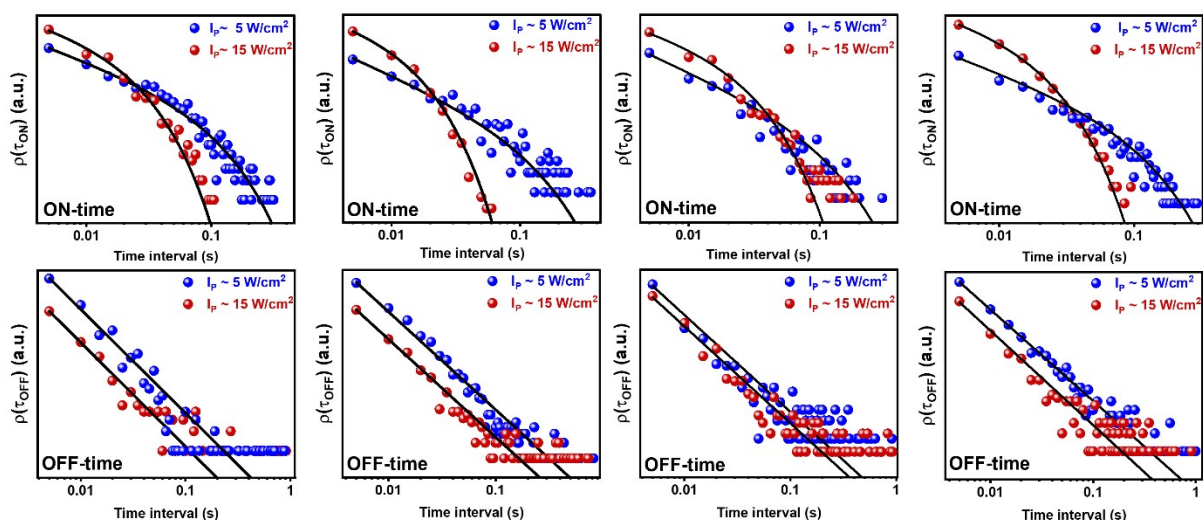
S7

Fig. S8 Few representatives of repetition data from the experiment shown in Fig. 6, with all experimental parameters maintained the same as in Fig. 6.
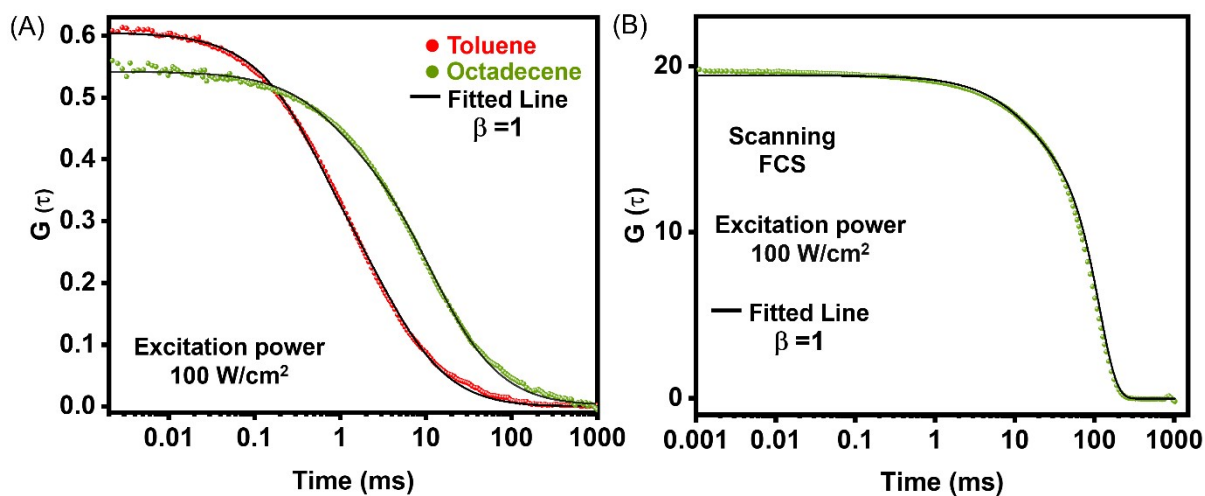

Fig. S9 (A-B) FCS (A) and sFCS (B) curves were fitted with Equation 2 (A) and Equation 1 (B), keeping β fixed at 1, resulting in unsatisfactory fittings. This is due to the distribution of τ_R, which cannot be described with β fixed at 1.
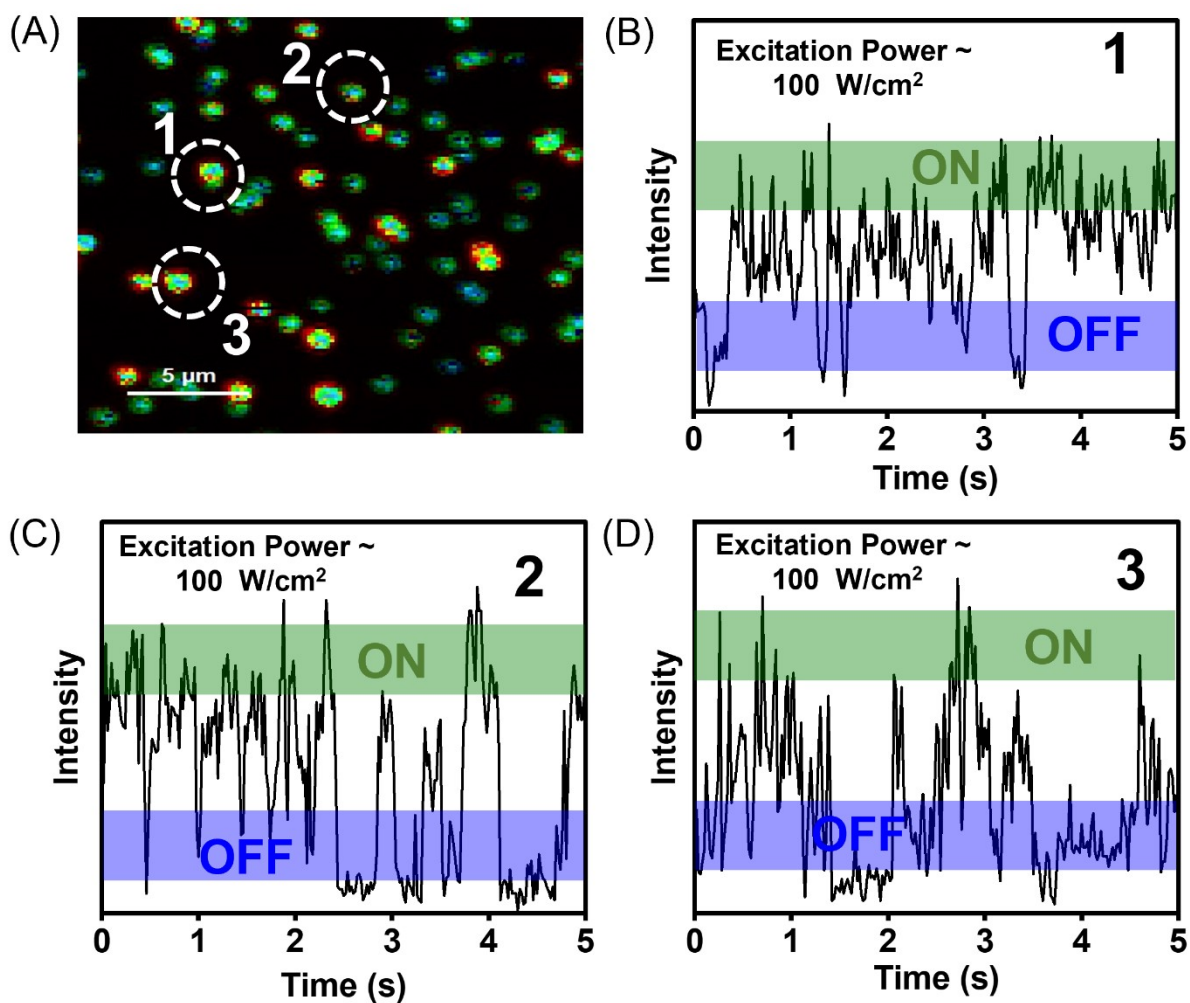
Fig. S10 Stability check for d-PNCs under high excitation power. (A) Confocal scanning image of d-PNCs embedded in a PMMA matrix under high excitation power (~100 W/cm², λex ~ 422 nm). (B-D) PL intensity time trajectories of individual PNCs, showing no signs of photobleaching for at least the first few seconds of high-power excitation. The numbers in the corners correspond to the particles with the same numbers in Figure A. Note that stability of a few seconds is significantly longer compared to the few hundreds of milliseconds scanning timescales (τ_S) of sFCS.

References

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