

Supporting Information for

Photoinduced Interfacial Electron Transfer from Perovskite Quantum Dots to Molecular Acceptors for Solar Cells

Bhagyashree Mahesha Sachith,^{a,‡} Zhijing Zhang,^{a,‡} Palyam Subramanyam,^{a,b,*} Challapalli

Subrahmanyam,^c Akihiro Furube,^d Naoto Tamai,^e Takuya Okamoto,^{a,b} Hiroaki Misawa,^{a,f}

Vasudevanpillai Biju^{1,2,*}

^aGraduate School of Environmental Science, Hokkaido University, N10W5, Sapporo, Hokkaido 060-810, Japan; ^bResearch Institute for Electronic Science, Hokkaido University, N20, W10, Sapporo, Hokkaido 001-0020, Japan; ^cIndian Institute of Technology Hyderabad, Kandi, Telangana 502285, India; ^dInstitute of Post-LED Photonics, Tokushima University, 2-1, Minamijosanjima-cho, Tokushima, 770-8506, Japan; ^eDepartment of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan; ^fCenter for emergent Functional Matter Science National Yang Ming Chiao Tung University Hsinchu, 30010 (Taiwan)

[‡]Equal contribution.

Corresponding authors: biju@es.hokudai.ac.jp, subbu@es.hokudai.ac.jp

Experimental Section

Materials

Chemicals. Cesium bromide (CsBr, >98%), methylammonium bromide (CH₃NH₃Br, MABr, >98%), lead bromide (PbBr₂, ≥98%), cesium acetate (CsAc, ≥98%), hexadecyl amine (HDA, >95%), oleic acid (>85%), hexadecene (>95%) and γ -butyrolactone (GBL, >99%), dehydrated toluene and *N, N*-dimethylformamide (DMF) were obtained from Fujifilm Wako. These reagents and solvents were used as received without further purification.

Synthesis of C-PQDs. We synthesized C-PQDs by a hot injection method by following a literature report.¹ Briefly, a mixture of PbBr₂ (210 mg, 0.564 mmol), oleic acid (1.6 mL, 5 mmol), hexadecyl amine (1.0 g, 4.15 mmol), and 1-hexadecene (25 mL) was placed in a reaction flask and dehydrated at reduced pressure for 1 h at 120 °C. In parallel, we prepared a CsAc solution (30 mg, 0.15 mmol) in 1-hexadecene (1.2 mL) and oleic acid (180 µL) at 120 °C. During drying, argon was flashed alternated with a vacuum every 20 minutes. After the lead salt was dissolved completely, we increased the lead salt solution temperature to 170 °C while maintaining an argon atmosphere. At this temperature, the CsAc solution was injected into the lead salt solution. Immediately, the reaction mixture was cooled by dipping it in an ice-water bath. The PQDs precipitated with *n*-hexane were washed with *n*-hexane. The particles were collected by centrifugation at 14000 rpm (5 min). Finally, the obtained residue resuspended in toluene was used in further studies.

Synthesis of L-PQDs. The LARP technique was employed to synthesize L-PQDs.² Briefly, a mixture of MABr (28 mg, 0.25 mmol), PbBr₂ (100 mg, 0.27 mmol), hexadecyl amine (HDA, 46 mg, 0.19 mmol), oleic acid (80 µl), and dry DMF (1 mL) was prepared, and it was stirred at 60 °C. The clear reaction mixture was later injected into vigorously stirring toluene (50 ml). Immediately, the reaction mixture turned green and gradually precipitated by turning into a turbid orange solution under vigorous stirring for 10 min. The precipitated PQDs were collected by centrifugation at 12,000 rpm for 5 min, and the supernatant was discarded. The precipitated PQDs were resuspended in toluene. In this process, *n*-butanol was used to remove excess ligands.

Synthesis of W-PQDs. We synthesized the W-PQDs by a modified spray technique.³ Briefly, a clear precursor solution of MABr (0.5 M) and PbBr₂ (0.5 M) dissolved in 1:1 (v/v) dry DMF:γbutyrolactone was prepared. 1 mL of this solution was taken in a glass vial with a Teflon spray cap. This perovskite precursor solution was spray-casted onto a glass coverslip stored in a plastic bag under the ambient atmosphere. The densities and sizes of the droplets and W-PQDs were controlled by adjusting the spraying rate and the distance between the sprayer and the coverslip substrate. We found 20 to 30 PQDs per 50 x 50 µm² for samples prepared by maintaining the sprayer-substrate distance at 15 cm.

Methods

Absorption and PL measurements. Stock solutions of the synthesized C-PQDs and L-PQDs were diluted with toluene and characterized using a fluorescence spectrometer (Hitachi F-4500, Japan) and a UV-vis spectrophotometer (Thermo Scientific Evolution 220). Ensemble fluorescence spectra were recorded by exciting the samples at 400 nm. The same fluorescence spectrometer was used for ensemble fluorescence quenching studies with different concentrations of TCNB/TCNQ.

TEM measurements. TEM samples were prepared by drop-casting the C-PQDs or L-PQDs solutions on TEM Cu100P grids, and W-PQDs were directly prepared on the TEM grid by the spray method discussed above. The grids were dried under a vacuum for 12 h, and TEM images were obtained using a Hitachi HD-2000 instrument operating at 200 kV.

Single-PQD PL measurements. C-PQDs or L-PQDs samples were prepared on glass coverslips (25×50 mm²) by a drop-drag method. W-PQDs were directly prepared on glass coverslips. PQD samples overlaid with a thin 1-hexadecene layer were mounted on a microscope stage, and PL intensity trajectories of single PQDs were recorded at a 33 ms frame rate. Single-PQD images and PL intensity trajectories were recorded using an EMCCD camera (iXon, Andor Technology) connected to the microscope (IX70, Olympus). PQDs were excited with a 404 nm diode laser (ThorLabs, 6.5 mW). The laser was controlled by a power supply (LDC210C, ~400 mA) and a temperature controller (TED200C, ~12-13 °C). The PL signals from the PQDs were collected using a 40x Olympus objective lens (NA = 0.60) and passed a 480 nm long-pass filter.

PL lifetime measurements. We used a fluorescence microscope for PL decay measurements, and the sample was excited with a picosecond (ps) laser (Advanced Laser Systems, 465nm, 45 ps, 1 MHz). PL decays were collected with a TCSPC assembly composed of an APD (Perkin Elmer, SPCM-AQRH) and a TCSPC module (Becker & Hickl GmbH, SPC-830). The picosecond laser intensity was decreased during PL decay measurements using ND filters. The detection field was restricted by an iris placed in front of the photodetector to collect PL from a selected PQD. We used a different TCSPC (nanosecond, Hamamatsu M12977, Quantaaurus-Tau) system for recording PL decays of PQD solutions.

DPV measurements. We estimated the oxidation potentials of the donors (C-PQDs and LPQDs) and the reduction potentials of the acceptors (TCNQ and TCNB) using differential pulse voltammetry (DPV, Figure S1). In a conventional three-electrode system, a glassy carbon (GC) disk, a non-aqueous Ag/AgNO₃ electrode, and a Pt wire were used as the working, reference, and counter electrodes, respectively. A 0.1 M TBAPF₆/THF solution was used as the supporting electrolyte, and all samples were recorded at 100 mV s⁻¹. Before each measurement, the GC working electrode was polished with 0.3 μm alumina paste, rinsed with acetone, and dried. For calibration to the standard hydrogen electrode (NHE) scale, 0.1 mM ferrocene was added after each measurement, and a ferrocene/ferrocenium (Fc/Fc⁺) couple was used as the internal standard.

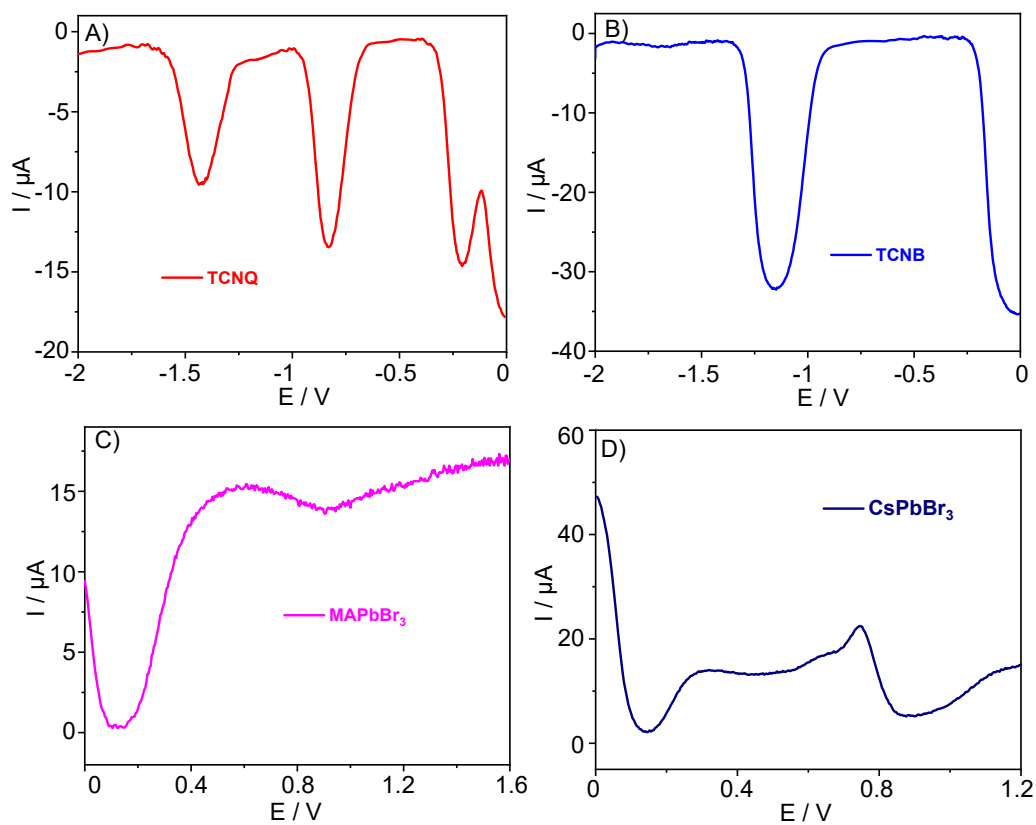


Figure S1. Oxidation and reduction potentials. DPV of (A) TCNQ, (B) TCNB, (C) MAPbBr₃ and (D) CsPbBr₃.

PL decays fitting:

The PL decay profiles were fitted using the third exponential equation (1):

$$\gamma(t) = \alpha_0 + \alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} + \alpha_3 e^{-t/\tau_3} \quad (1)$$

where τ_n ($\tau_1/\tau_2/\tau_3$) signifies the lifetime component and α_n ($\alpha_1/\alpha_2/\alpha_3$) the amplitudes. α_0 is a constant.

One lifetime component comes from the band-to-band recombination (a radiative relaxation), and the rest from nonradiative recombination. The average PL lifetimes of the single dots were obtained by using equation (2):

$$\Sigma \alpha_n \tau_n / \Sigma \alpha_n \quad (2)$$

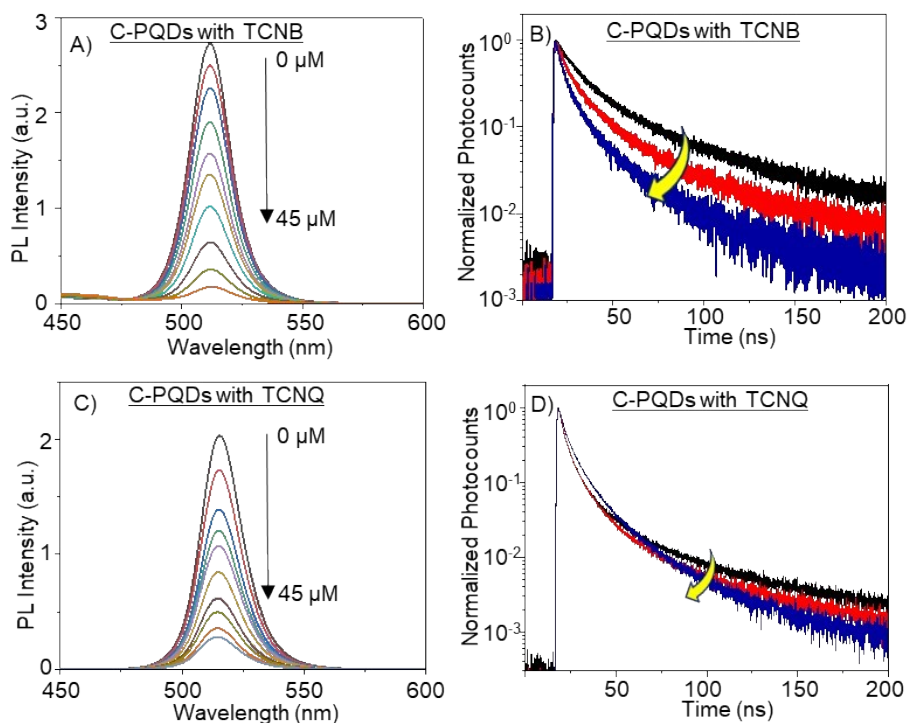


Figure S2. PL quenching in the solution phase. (A, B) PL spectra and (C, D) PL decay profiles of C-PQD solutions supplemented with (A, C) TCNB or (B, D) TCNQ (λ_{ex} : 400 nm). The quencher concentration was increased from 0 to 45 μM @ 5 μM during the PL spectral measurements and from 0 to 20 μM @ 10 μM during the PL decay measurements.

Table S1. Triexponentially fitted average PL lifetimes for L-PQDs and C-PQDs without or with TCNB/TCNQ.

TCNB/TCNQ Concentration [Q] (μM)	L-PQDs/TCNB τ_{av} (ns)	L-PQDs/TCNQ τ_{av} (ns)	C-PQDs/TCNB τ_{av} (ns)	C-PQDs/TCNQ τ_{av} (ns)
0	30.7	29.8	11.3	9.9
4.9	20.0	22.7	10.4	9.0
9.8	12.8	15.7	8.9	8.7
14.7	8.9	12.6	7.7	8.1
19.6	6.2	9.9	5.0	7.2

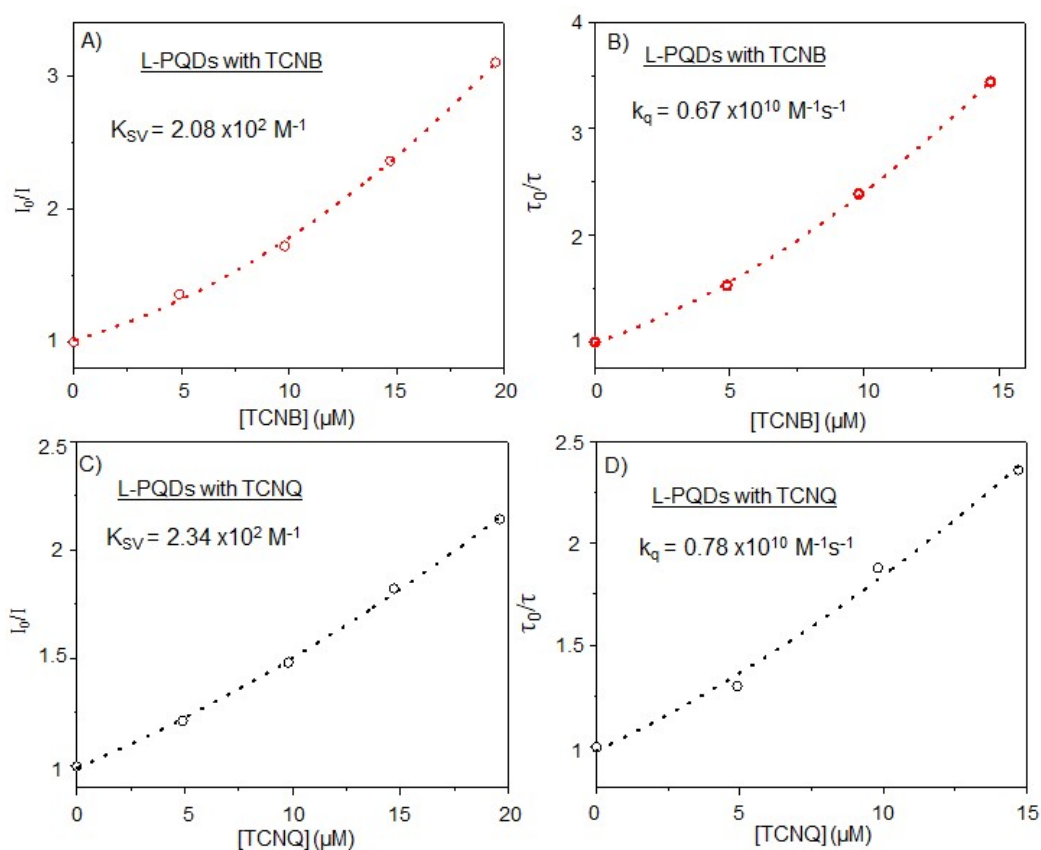


Figure S3. S-V plots for L-PQDs with TCNB or TCNQ. (A) I_0/I vs TCNB concentration, (B) τ_0/τ vs TCNB concentration, (C) I_0/I vs TCNQ concentration, and (D) τ_0/τ vs TCNQ concentration.

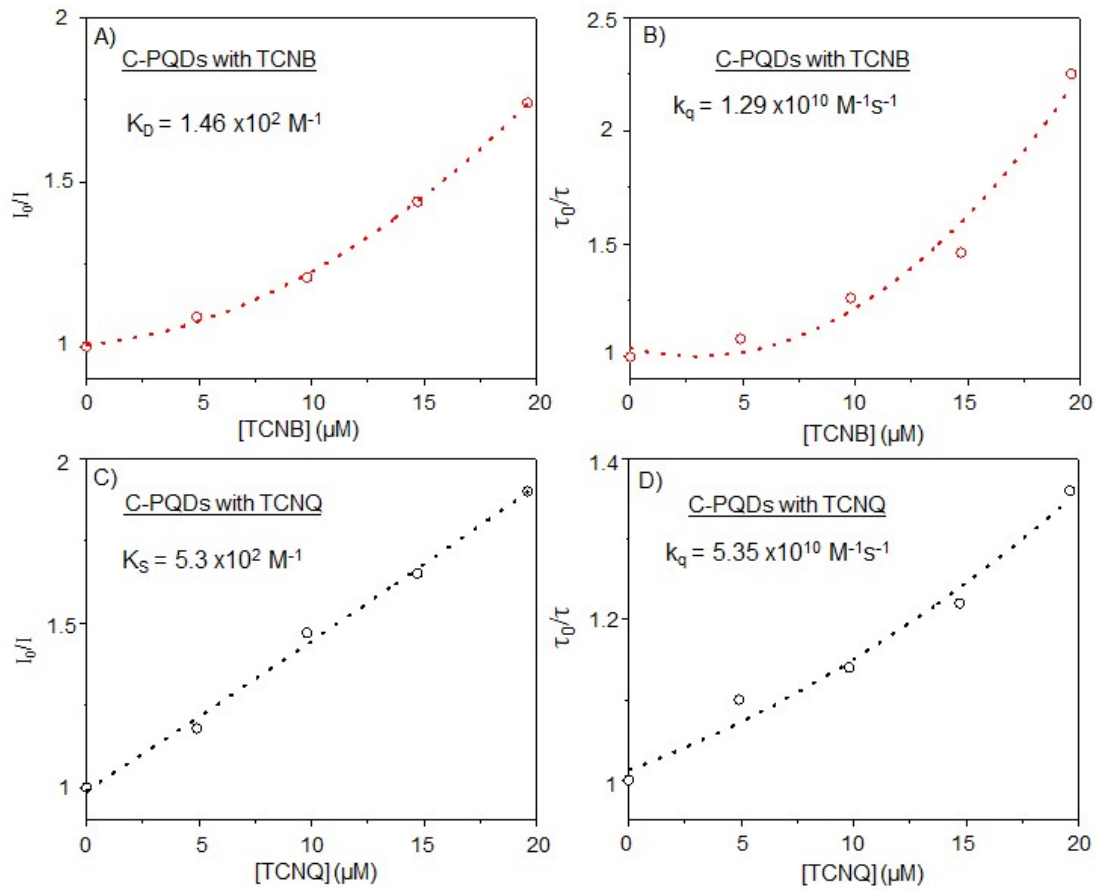


Figure S4. S-V plots for C-PQDs with TCNB or TCNQ. (A) I_0/I vs TCNB concentration, (B) τ_0/τ vs TCNB concentration, (C) I_0/I vs TCNQ concentration, and (D) τ_0/τ vs TCNQ concentration.

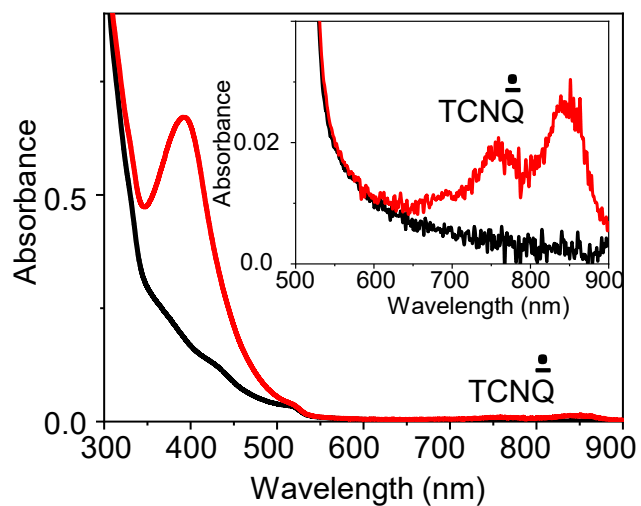


Figure S5. The charge-separated state. Steady-state absorption spectra of L-PQDs without or with TCNQ (inset: zoomed-in spectra from 500 to 900 nm showing the TCNQ \cdot^-). [(Black spectrum: L-PQDs, Red spectrum: L-PQDs with TCNQ (1 mM)].

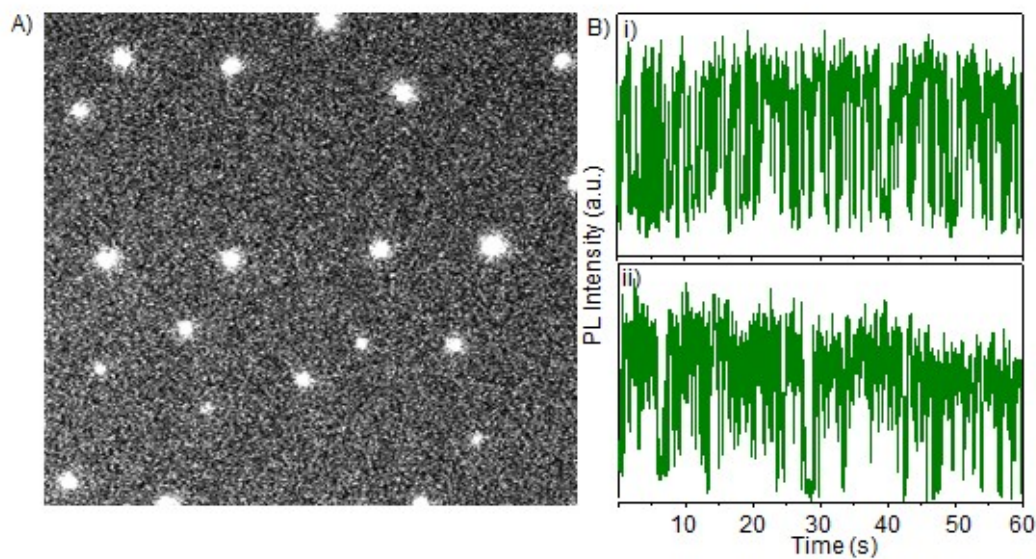


Figure S6. Properties of single PQDs. (A) PL image of C-PQDs tethered on glass substrate photoexcited with the 404 nm laser. (B) PL intensity trajectories of two pristine C-PQDs.

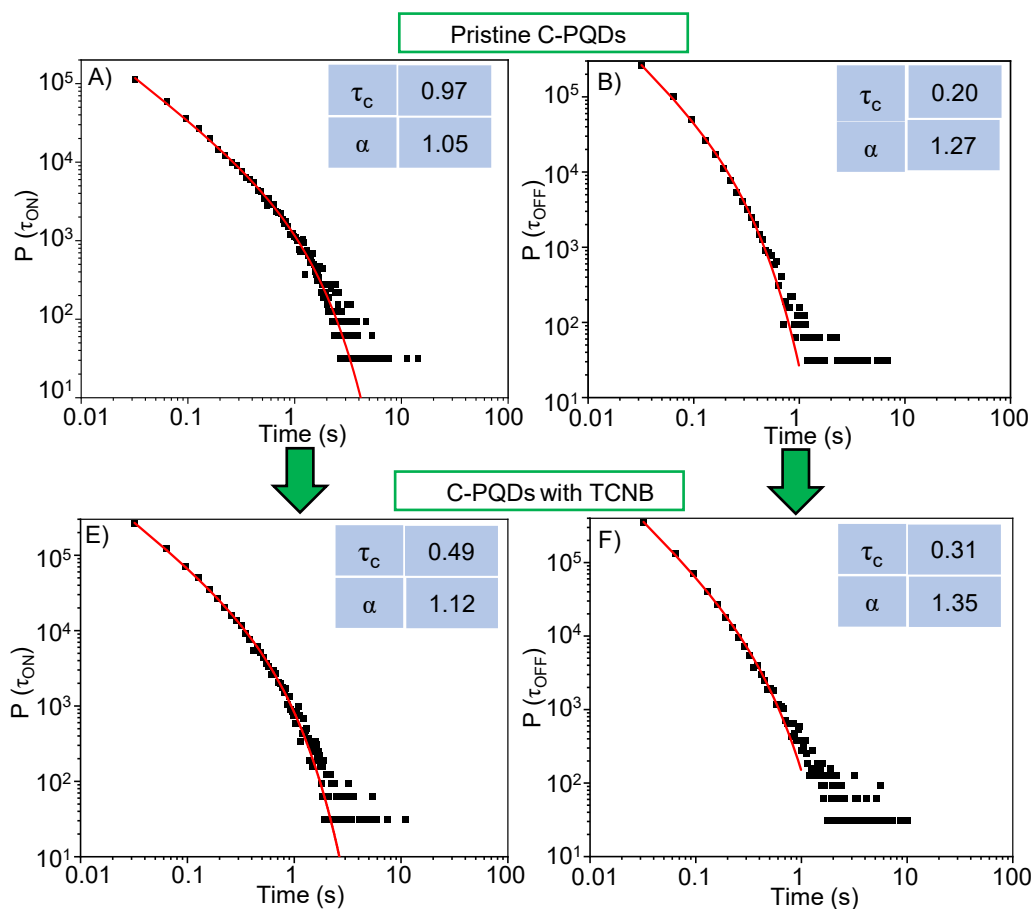


Figure S7. ON-/OFF-time probability distributions. Log-log distributions of (A, C) ON-time and (B, D) OFF-time probabilities for C-PQDs (A, B) without or (C, D) with TCNB.

References

1. Q. A. Akkerman, V. D’Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato and L. Manna, *J. Am. Chem. Soc.*, 2015, **137**, 10276–10281.
2. L. Chouhan, S. Ito, E. M. Thomas, Y. Takano, S. Ghimire, H. Miyasaka and V. Biju, *ACS Nano*, 2021, **15**, 2831–2838.
3. A. P. Pushkarev, V. I. Korolev, D. I. Markina, F. E. Komissarenko, A. Naujokaitis, A. Drabavičius, V. Pakštas, M. Franckevičius, S. A. Khubezhov and D. A. Sannikov, *ACS Appl. Mater. Interfaces*, 2019, **11**, 1040–1048.