SUPPORTING INFORMATION

Instantaneous, room-temperature, open-air atmosphere, solution-phase synthesis of perovskite quantum dots through halide exchange employing non-metal based inexpensive HCl/HI: ensemble and single particle spectroscopy**

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CONTENTS

I. Experimental Section.

a. Chemicals.

Cesium bromide (99.9%), lead bromide (99.9%), oleic acid (90%), oleylamine (70%), toluene (99.8%), Octane (99%) Hydriodic acid (57 weight % in H_2O) were procured from Sigma Aldrich. N,N-dimethylformamide (DMF,90%), hydrochloric acid (HCl, 35 weight % in H_2O) and hydrobromic acid (HBr, 47 weight % in water) were obtained from Merck. All the chemicals were used without any further treatment.

b. Synthesis Procedure.

In a typical synthesis of $CsPbBr_3$, $PbBr_2$ (0.2 mmol) and CsBr (0.2 mmol) were dissolved in 5 mL N,N-Dimethylformamide (DMF). As ligands 0.5 mL Oleic acid (OA) and 0.2 mL Oleyl amine (OAm) were added to the precursor solution. Then, 0.05 mL of this precursor solution was quickly added into 5 mL of toluene under vigorous stirring at room temperature. A bright green emission was observed instantaneously after the addition which indicates the formation of $CsPbBr_3$ PQDs. The formation of the nanocrystals is based on the fact that inorganic salts are highly soluble in DMF (~ 0.2 g/mL) but they are less soluble in toluene (~ 10^{-7} g/mL).[1] This drastic drop in solubility (more than six orders in magnitude) immediately forms a supersaturated state when the precursor solution is added into the toluene leading to the formation of nanocrystals in presence of external perturbation (stirring of bar magnet).

For the synthesis of $CsPb(Br/Cl)_3$ mixed halides 25 μL Hydrochloric acid was diluted in 10 mL of DMF solution. Different amount of this solution was added quickly to the previously synthesised $CsPbBr_3$ solution dispersed in toluene at room temperature under vigorous stirring. The halide exchange takes place immediately after the addition of HCl solution. The movie in S1 shows the instantaneous formation of mixed $CsPb(Br/Cl)_3$.

(S1: Movie for $CsPb(Br/Cl)_3$ synthesis)

Similarly for $CsPb(Br/I)_3$ mixed halide synthesis 25 μL Hydriodic acid was diluted in 10 mL of DMF solution. This solution was then added in different amount to a $CsPbBr_3$ solution dispersed in toluene at room temperature under vigorous stirring. The movie in S2 shows the instantaneous formation of mixed $CsPb(Br/I)_3$

(S2: Movie for $CsPb(Br/I)_3$ synthesis)

We would like to mention here that unlike hot injection synthesis, in our synthesis of $CsPbBr_3$ and the halide exchanged PQDs, no condensation/precipitation of the PQDs could be observed. $CsPbBr_3$ and the halide exchanged PQDs were purified via high speed centrifugation at 12000 rpm for 30 min followed by re-dispersion in toluene.[1-3] Moreover, we didn't observe any detrimental effect of H^+ ion used (as HX, X=Cl or I) on the quality or stability of the halide exchanged PQDs.

c. Degree of Instantaneity: In our case halide source is dissolved in DMF. When this solution is added to toluene the halide exchange takes place instantaneously signifying the reaction starts within one second. However, when DMF solution is added to octane, it requires a few seconds for the completion of the halide exchange. This is perhaps because of the ease of miscibility of the solvent pairs. Therefore, by choosing a particular solvent pair the kinetics of halide exchange could be controlled. This is an interesting observation. Whether by changing the solvent pair the quality, size, optical properties etc. of the PQDs can be controlled or not needs to be explored in a detailed manner. Such experiments are currently underway.

II. Instrumentation.

TEM Analysis: TEM and High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were recorded with the JEM-2100F, JEOL operating at 200 kV acceleration voltage equipped with the energy dispersive analysis of X-rays (EDS) setup. A dilute solution of PQDs in toluene was drop casted over carbon-coated Cu grids and dried under vacuum.

PXRD Measurement: The X-ray diffraction (XRD) measurements were carried out using Cu Kα = 1.54059 Å radiation with a Rigaku powder X-ray diffractometer.

Steady State Optical Spectroscopic Measurements: Steady state absorption spectra have been recorded in CARY Bio 300 UV-Visible Spectrophotometer. Corrected PL emission spectra have been recorded with Fluoromax-3, Horiba Jobin Yvon spectrofluorimeter.

Time Resolved Optical Spectroscopic Measurements: Photoluminescence decay measurements were performed in time correlated single photon counting (TCSPC) module (Horiba Jibon Yvon IBH) using pico second pulsed lasers (λ_{ex} = 405 nm, fwhm < 100ps) as excitation sources and 50 ns TAC range. An MCP photomultiplier tube (PMT) (Hamamatsu R3809U-50 series) was used as the detector. A nonlinear least-squares iterative deconvolution procedure using IBHDAS6 (version 2.2) was employed to fit the decay curves using a suitable exponential decay equation. The amplitude averaged PL decay lifetime (τ_{avg}) was calculated for every PL decay using the following equation –

$$< \tau > \; = \frac{\sum_i B_i \tau_i^2}{\sum_i B_i \tau_i}$$

.... eq. (1)

where, τ_i is the excited state lifetime component and B_i is corresponding amplitude of decay components.[4-5]

III. Reversibility Test: In order to check the reversibility at first 25 μL Hydrobromic acid was diluted in 10 mL of DMF solution and it was then added to a previously synthesized $CsPb(Br/Cl)_3$ and $CsPb(Br/I)_3$ dispersed in toluene separately at room temperature and ambient condition.
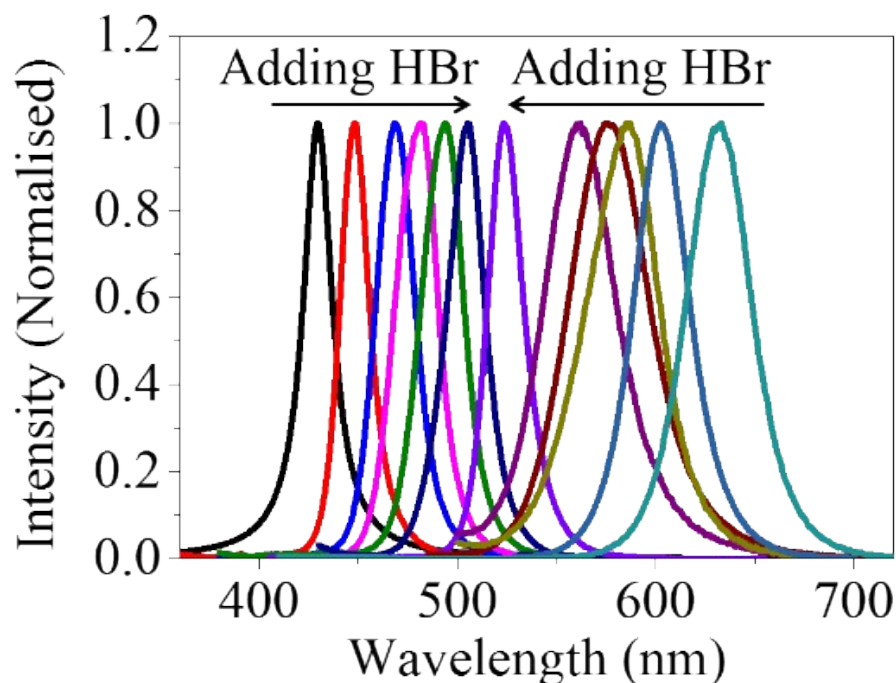
Fig. S3: Evolution of PL emission spectra after addition of HBr to mixed CsPb(Br/Cl)$_3$ and CsPb(Br/I)$_3$ PQDs.

IV. Stability Test in Open Air Atmosphere: Stability of the as synthesised PQDs were investigated in open air atmosphere condition dispersed in toluene and octane. Corrected PL intensity of the PQDs were recorded at different time intervals.
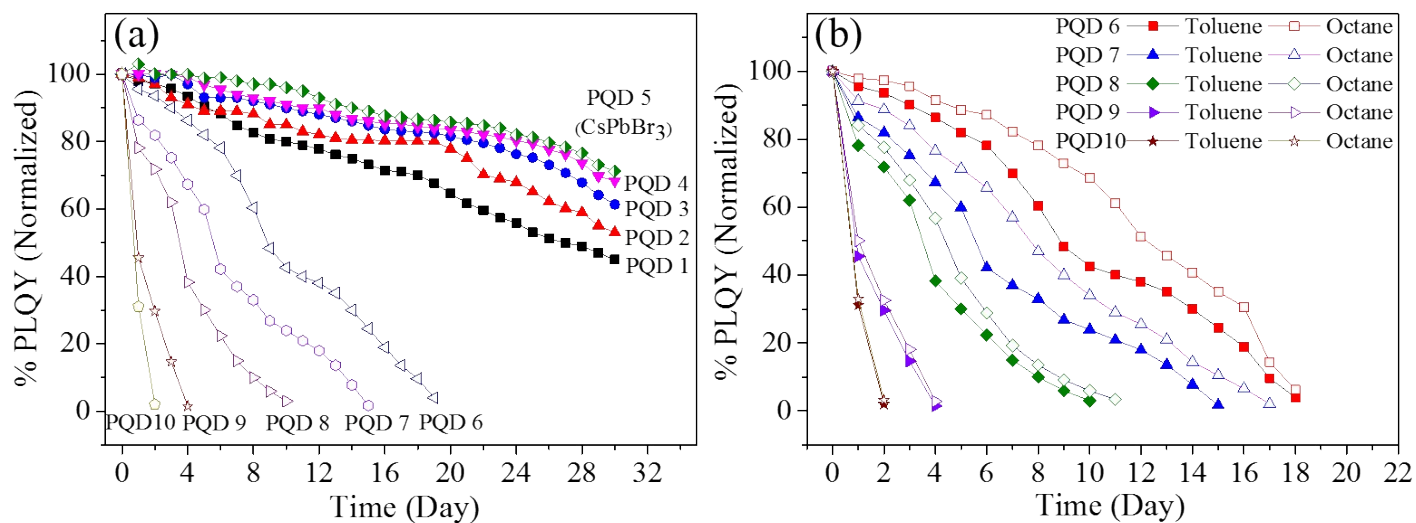

Fig. S4: Time dependent change of % PLQY (a) PQDs dispersed in toluene (b) Comparison with PQDs dispersed in octane.
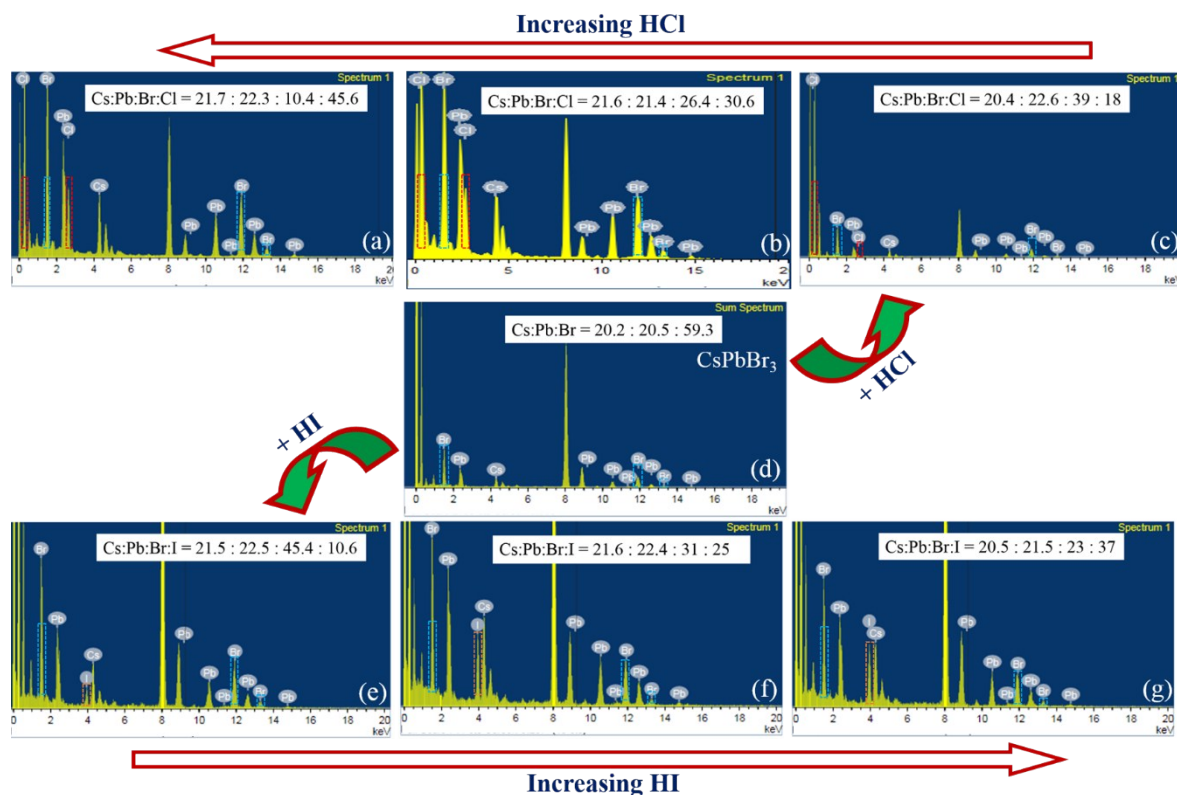
V. Elemental Characterization.

Fig. S5: EDAX spectra of CsPbBr$_3$ (d) along with CsPb(Br/Cl)$_3$ mixed PQDs (a,b,c) and CsPb(Br/I)$_3$ mixed PQDs (e,f,g). Atomic % of Cl and I increases with the increasing amount of HCl and HI to CsPbBr$_3$.
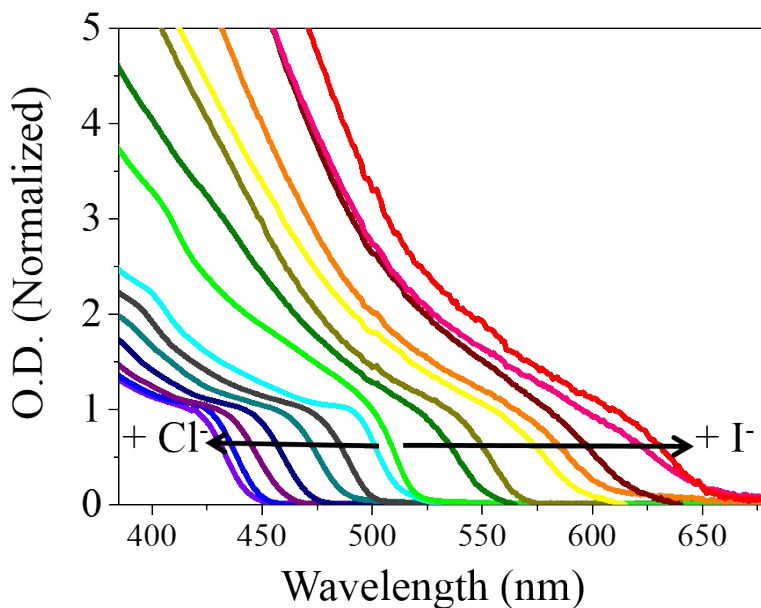
VI. Steady State Absorption Spectra.

Fig. S6: Shifting of absorption spectra after addition of HCl and HI to CsPbBr$_3$ solution.

VII. PL Quantum Yield Calculation: PLQY of all the compounds (PQD 1 to PQD 10) were calculated using relative quantum yield method using the following eq. 1, where Q, OD, I and n stand for quantum yield, optical density, integrated intensity, refractive index of the solvent respectively. Subscript R refers to the reference. O.D. of all the PQDs at each excitation wavelength has been kept at a value of 0.05 or lower. The references used in the experiment are Quinine Sulphate (PLQY 58% in 0.1 M H_2SO_4), Coumarin 153 (PLQY 58% in ethanol), Rhodamin 6G (PLQY 96% in ethanol).

$$\Phi = \Phi_R \frac{I\ OD_R n^2}{I_R\ OD\ n_R^2} \quad \ldots\ldots\ldots\ldots\ldots\text{eq. 2}$$

VIII. Table S1: Photophysical properties of pure and mixed halide PQDs in toluene.

Sample	Steady State			Time Resolved							
	λ_{ems}^{max} (nm)	FWHM (nm)	PLQY	τ_1 (ns)	B_1	τ_2 (ns)	B_2	τ_3 (ns)	B_3	τ_{avg} (ns)	χ^2
PQD-1	430	17	0.01	0.33	12.50	1.53	41.83	10.92	45.67	9.78	1.20
PQD-2	444	18	0.30	0.35	10.35	2.35	29.59	12.47	60.06	11.56	1.15
PQD-3	477	25	0.55	0.45	4.68	3.07	31.25	12.00	64.07	10.98	1.10
PQD-4	500	27	0.72	1.04	6.86	3.85	39.71	13.87	53.43	12.07	1.04
PQD-5	513	26	0.76	1.42	10.22	12.54	89.78			12.40	1.02
PQD-6	555	28	0.50	2.92	10.24	15.31	89.76			15.05	1.10
PQD-7	580	32	0.38	4.88	9.81	21.81	90.19			21.41	1.07
PQD-8	594	34	0.66	8.07	16.71	31.40	83.29			30.26	1.04
PQD-9	630	38	0.53	10.69	21.39	31.72	78.61			29.95	1.05
PQD-10	645	39	0.82	10.33	16.95	33.87	83.05			32.49	1.05

IX. Single Particle Investigation: In order to investigate the blinking behavior of single PQDs they were embedded in Poly (methyl methacrylate) (PMMA) matrix and spin coated on cleaned glass coverslip of 0.17 mm thickness. These single PQDs have been probed using our home-build Total Internal Reflection Fluorescence (TIRF) microscope using an oil-immersion objective (Zeiss, PlanApo, 100x, NA 1.46). All the PQDs were excited using 405 nm CW LASER (COHERENT CUBE). PL signal has been detected with an EMCCD camera (ANDOR iXON3) with 100 ms integration time and a suitable EM gain. At least 150 single particles for each set of PQDs were investigated. Widely separated single spots ensured measurement from single particles. The total intensity from each single particle has been obtained choosing a suitable region of interest and intensity – time trace has been obtained from each single particle. Blinking behavior has been observed from each single QDs and analyzed using a home written software in MATLAB. Histogram of the intensity of each time trace yielded a well separated bimodal distribution of

intensities. Hence it was quite convenient to put a well-defined threshold to separate high intensity PL signal from low intensity background. Anything above the threshold is considered to be ON and below the threshold limit is considered to be OFF. Upon thresholding the PL intensity time trace is converted into a sequence of ON- and OFF-events of given time durations. Using this thresholding-histogramming technique a distribution of ON- event durations have been generated from which ON fraction of these PQDs have been calculated. ON fraction of a single PQD is defined as the sum of the all ON event durations in a certain time trace measurement divided by the total event duration (i.e. sum of all ON and OFF event durations).

Blinking_Movie.avi

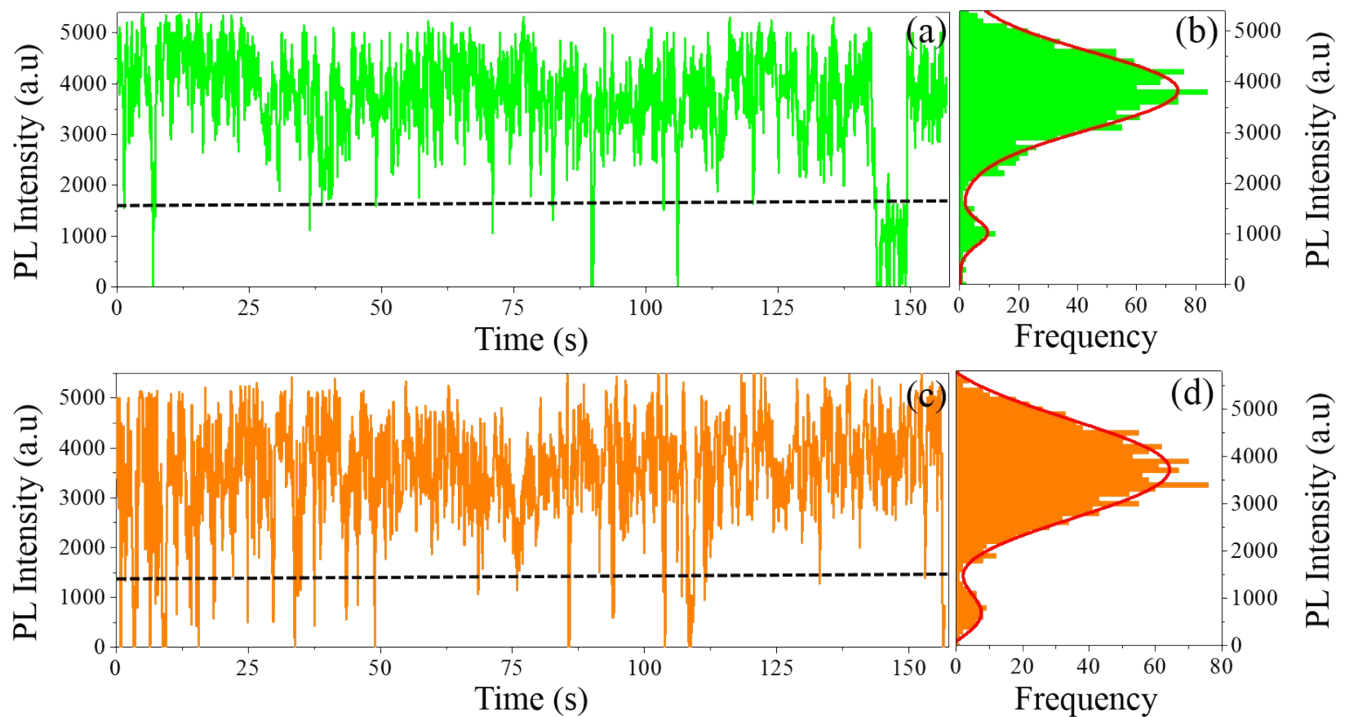**Fig. S7:** Movie showing the blinking of single PQDs.

Fig. S8: Single particle time trace and PL intensity histrogram for CsPbBr$_3$ (PQD 5) (a,b) and for CsPb(Br/I)$_3$ mixed halide (PQD 6) (c,d).

X. Equations used in blinking dynamics analysis:

$$P_{event} = a.t_{event}^{-m} \quad Power\ law$$

$$P_{event} = a.t_{event}^{-m}.e^{-k.t_{event}} \qquad \textit{Truncated power law}$$

XI. Comparison of fitting for ON and OFF probability density with different equations.
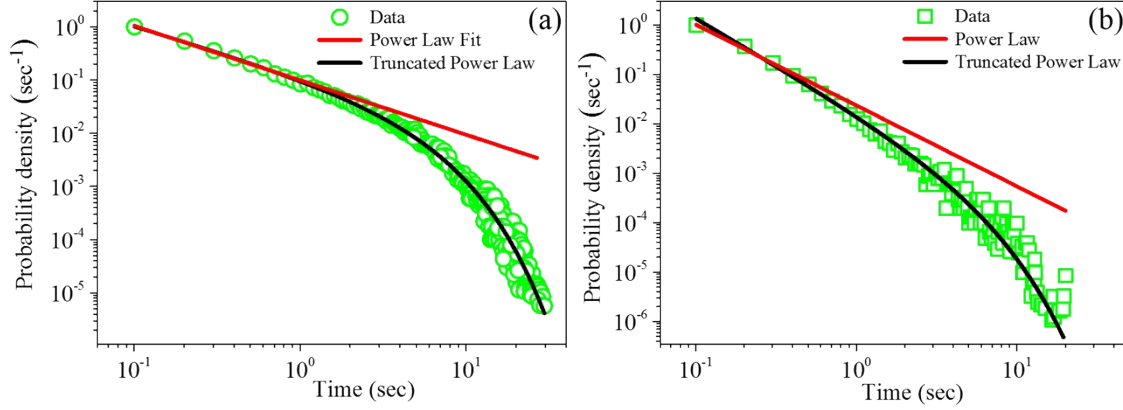

Fig. S9: (a) ON-time probability density distribution plot and (b) OFF- time probability density distribution plot of CsPbBr$_3$ PQD using different fitting equations.

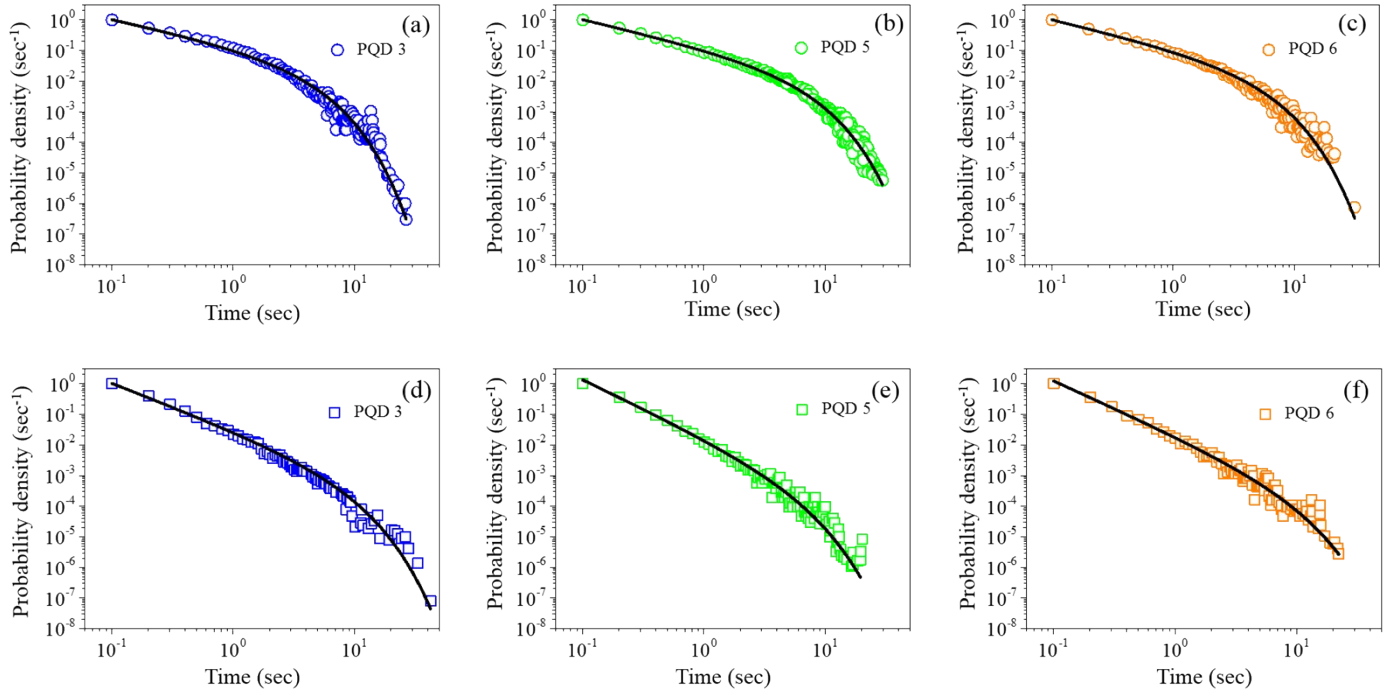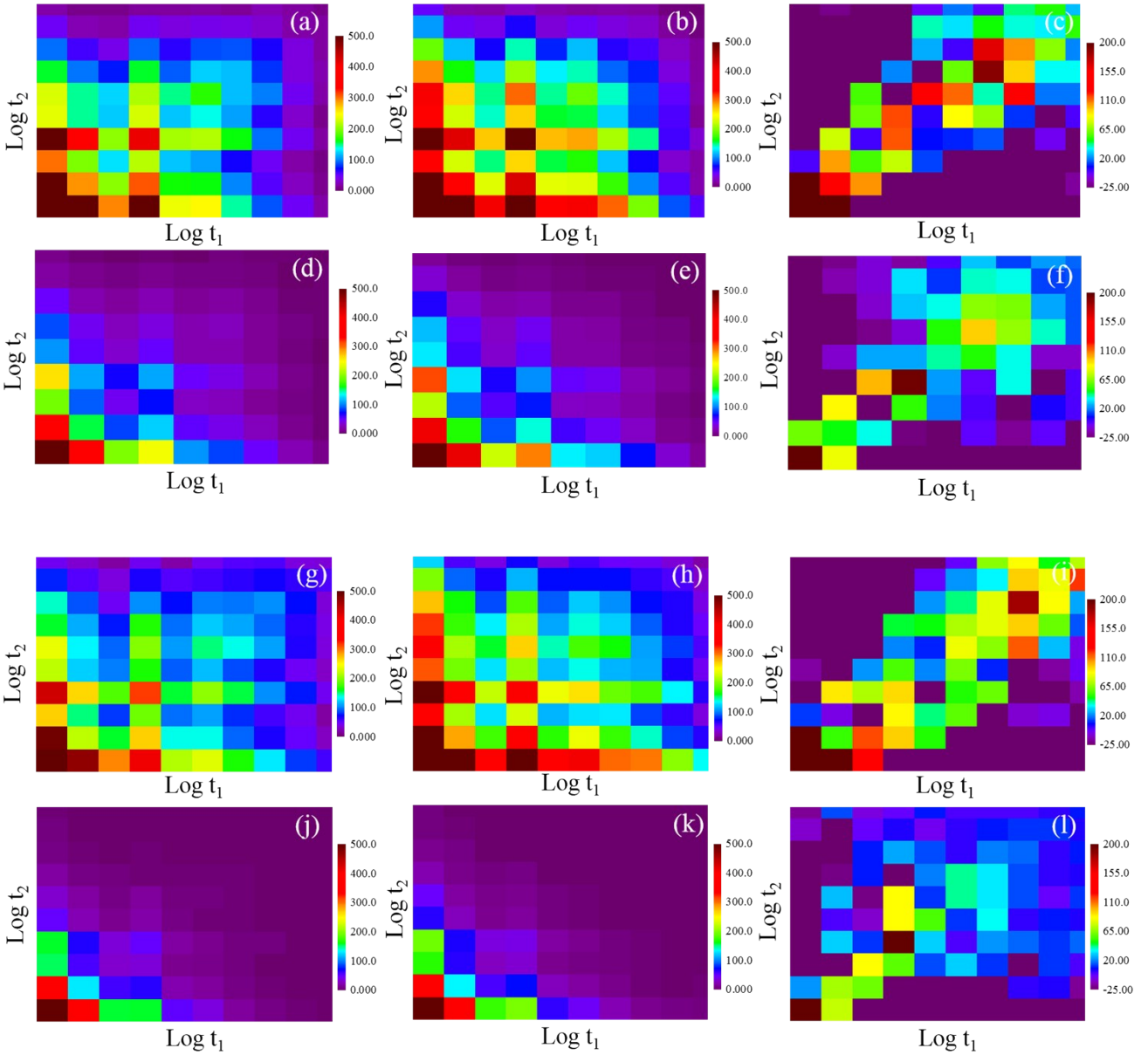**XII. Probability density distribution plot for all three PQDs.**

Fig. S10: Probability density distribution of (a,b,c) ON event durations and (d,e,f) OFF event durations of PQD 3 (blue), PQD 5 (green) and PQD 6 (orange).

XIII. 2D joint probability distribution analysis for PQD 3 (a-f), PQD 5 (g-l) and PQD 6 (m-r) respectively.
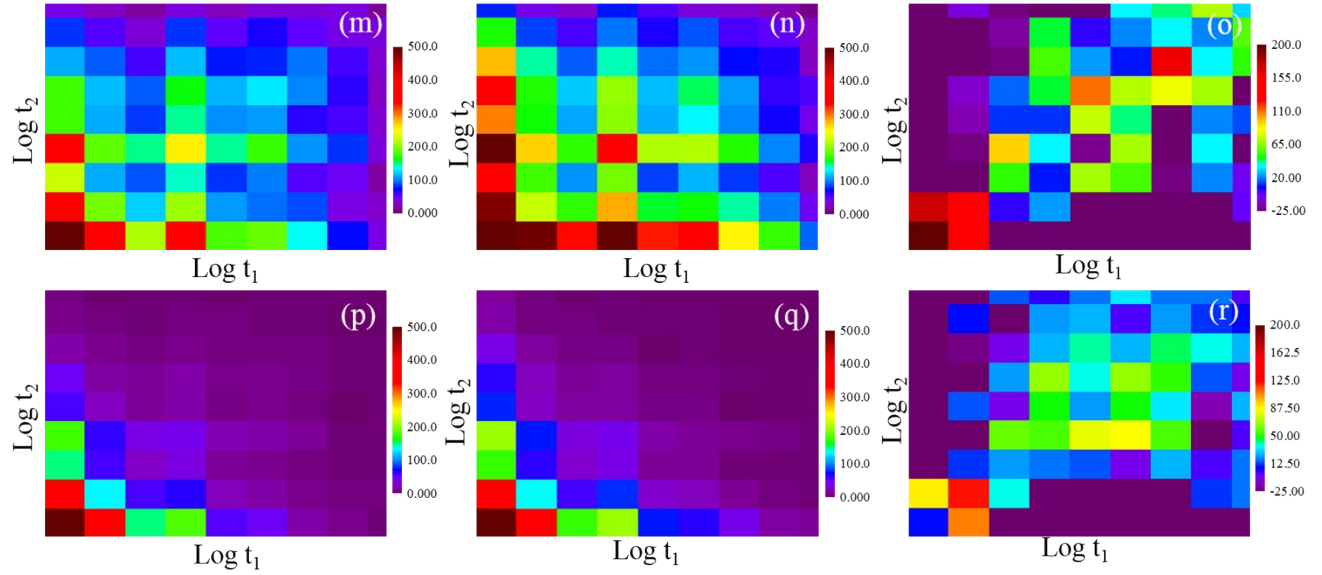
Fig. S11. 2D joint probability distributions for two adjacent ON-event durations (a) PQD 3, (g) PQD 5, (m) PQD 6. [for two adjacent OFF-event durations (d) PQD 3, (j) PQD 5, (p) PQD 6.]. 2D joint probability distributions for two ON-event at a larger separation (fifty intervals) (b) PQD 3, (h) PQD 5, (n) PQD 5. [for two OFF-event at a larger separation (fifty intervals) (e) PQD 3, (k) PQD 5, (q) PQD 6.]. Two dimensional difference histogram for ON-event durations (c) PQD 3, (i) PQD 5, (o) PQD 6. [for OFF-event durations (f) PQD 3, (l) PQD 5, (r) PQD 6.]

XIV. Table S2: Pearson's correlation coefficient (R) of different PQDs.

Sample	R_{log} (two adjacent ON)	R_{log} (two adjacent OFF)	R_{log} (ON and OFF)
PQD 3	0.252	0.169	-0.016
PQD 5	0.287	0.167	-0.023
PQD 6	0.254	0.221	-0.049

XV. References:

1. X. Li, Y. Wu, S. Zhang, B. Cai, Y. Gu, J. Song, H. Zeng, *Adv. Funct. Mater.* **2016**, *26*, 2435-2445.

2. C. Bi, S. Wang, W. Wen, J. Yuan, G. Cao, J. Tian, *J. Phys. Chem. C* **2018**, *122*, 5151-5160.

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