Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

Transforming Exciton Dynamics in Perovskite Nanocrystal through Mn Doping

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CONTENTS

I. Experimental Section

a. Chemicals used

Cesium carbonate (Cs_2CO_3, 99%), Oleylamine (OAm, 70%), Stearic acid (SA, 95%), 1-Octadecene (ODE, 90%), Lead chloride ($PbCl_2$, 99%), Zinc bromide ($ZnBr_2$, 98%), Manganese chloride ($MnCl_2$, 99%), Hydrobromic acid (HBr in 47% water), Ethanol, Diethylether (>99%), Toluene (>99.5%), Concentrated HCl (35%) and Concentrated HNO_3 (69%) were procured from Sigma-Aldrich. All the reagents were used as received from Sigma-Aldrich without further purification.

b. Synthesis procedure

Preparation of cesium stearate (Cs-stearate)

81 mg Cs_2CO_3 (0.25 mmol), 225 mg SA and 4 mL ODE were loaded into a 100 mL two neck round bottom flask and heated to 100°C under vacuum for 1 hour. The mixture was further heated to 140°C under N_2 flow and kept for 1 hour until a clear solution was obtained.

Preparation of oleylammonium bromide (OAmBr)

2.5 mL OAm, 0.9 mL HBr and 20 mL ethanol were loaded into a 100 mL round bottom flask. This mixture was stirred for 12 hours in ice water bath under nitrogen atmosphere. Ethanol was evaporated to get a white precipitate. Then the precipitate was washed with diethyl ether and finally diethyl ether was evaporated to get the dried product of OAmBr. Finally OAmBr solution was prepared by adding OAmBr salt in requisite amount of toluene. This OAmBr solution was further used for halide exchange reaction.

Preparation of Zn alloyed $CsPb(Cl/Br)_3$ PNC

Zn alloyed $CsPb(Cl/Br)_3$ have been synthesized following a modified literature procedure.[1] 35 mg $PbCl_2$ (0.12 mmol), 14 mg of $ZnBr_2$ (0.06 mmol) [Pb:Zn molar ratio = 2:1], 450 mg SA, 0.5 mL OAm and 5 mL ODE were loaded into a 100 mL three neck round bottom flask and heated to 100°C under vacuum for 1 hour. Then the temperature was raised to 160°C under N_2 flow. 0.4 mL Cs stearate solution was then hot injected into the solution and the solution was quickly cooled down (within 5 second) to room temperature in an ice water bath. After purification the PNC was dispersed in toluene and then OAmBr was treated to get the desired Zn alloyed $CsPb(Cl/Br)_3$ mixed halide PNC.

Preparation of Zn alloyed Mn doped $CsPb(Cl/Br)_3$ PNC

Zn alloyed Mn doped $CsPb(Cl/Br)_3$ have been synthesized following a modified literature procedure.[1] 55 mg $PbCl_2$ (0.2 mmol), 23 mg of $ZnBr_2$ (0.1 mmol), 50 mg $MnCl_2$ (0.4 mmol) [Pb:Zn:Mn molar ratio = 2:1:4], 450 mg SA, 0.5 mL OLA and 5 mL ODE were loaded into a 100 mL three neck round bottom flask and heated to 100°C under vacuum for 1 hour. Then the temperature was raised to 160°C under N_2 flow. 1.25 mL Cs stearate solution was then hot injected into the solution and the solution was quickly cooled down (within 5 second) to room temperature in an ice water bath. After purification the PNC was dispersed in toluene

and then OAmBr was treated to get the desired Zn alloyed Mn doped $CsPb(Cl/Br)_3$ mixed halide PNC.

c. Purification

The PNCs were purified by centrifuging at 10000 rpm for 20 minutes, the supernatant was then discarded which contain unreacted precursor and by-products and the precipitate was re-dispersed in toluene. Further characterization and experiments were done by this purified PNCs.

II. Instrumentation

TEM Measurement

Transmission Electron Microscopy (TEM) images were recorded with the JEM-2100F, JEOL operating at 200 kV acceleration voltage. Dilute solutions of PNCs in toluene were drop casted over a carbon-coated Cu grid and dried under vacuum for overnight.

PXRD Measurement

The powder X-ray diffraction (PXRD) measurements for all the PNCs 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 3500 UV-Vis Compact Spectrophotometer. PL emission spectra have been recorded with Fluoromax-4, Horiba Jobin Yvon spectrofluorimeter. Temperature dependent PL emission spectra has been measured using FLS 1000 spectrofluorimeter.

Time Resolved Optical Spectroscopic Measurements

Time-resolved nanosecond (ns) PL decay measurements were performed using the time correlated single-photon-counting module (Horiba Jobin Yvon IBH). Picosecond pulsed laser (λ_{ex} = 405 nm, FWHM < 200 ps) with a repetition rate of 1 MHz were used as excitation sources, and an MCP photomultiplier tube (PMT) (Hamamatsu R3809U-50 series) was used as the detector. Time resolved PL decay traces have been collected monitoring at their respective emission maximum. PL decays have been observed to be multi exponential in nature and all these PL decays can be fitted with a triexponential decay function mentioned below:

$$I_t = I_0 \sum_{i=1}^{3} A_i \; e^{-\frac{t}{\tau_i}} \qquad (1)$$

where, I_t and I_0 represent PL intensity of the sample at time 't' and at time zero respectively, τ_i represents time associated with an individual decay component and A_i represents the amplitude associated with that channel. A nonlinear least-squares iterative reconvolution procedure[2] using IBHDAS6 (version 2.2) was employed to fit the decay curves using a suitable exponential decay equation. Average lifetime can be calculated using the formula:

$$<\tau> = \frac{A_1\tau_1^2+A_2\tau_2^2+A_3\tau_3^2}{A_1\tau_1+A_2\tau_2+A_3\tau_3} \quad (2)$$

The quality of the fit was assessed from the χ^2 values (1 ± 0.2) and the distribution of the residuals.

Time-resolved microsecond (µs) to millisecond (ms) PL decay measurements for Mn emission in Zn alloyed Mn doped $CsPb(Cl/Br)_3$ were performed using FLS 1000 spectrofluorimeter.

III. Zn Doping Induced Enhancement of Optical Properties in PNCs

Zn doping has been used as a strategy to enhance the optical properties of the PNCs in previous literatures. We have tabulated here that how Zn doping induced enhancement of optical properties could be observed in PNCs.

Table S1. Zn doping induced enhancement of optical properties in PNCs.

Properties	Reference
Through Zn doping PLQY of blue emitting $CsPbCl_3$ PNC could be enhanced to as high as 85%, with enhanced thermal stability.	*ACS Appl. Nano Mater*., 2020, **3**, 7621−7632
Through Zn doping defect tolerance of $CsPbBr_3$ PNC could be enhanced.	*J. Phys. Chem. Lett*., 2021, **12**, 3393–3400
Through Zn doping in $CsPbBr_3$ PNC a high PLQY of 91%, narrower FWHM of PL emission (15.5 nm) and with enhanced thermal and ambient air stability could be achieved.	*J. Alloys Compd*., 2021, **866**, 158969
For $CsPbI_3$ PNC PLQY has been improved (from 61% to 98%) through Zn doping.	*Nano Lett*., 2019, **19**, 1552-1559
Through Zn doping PLQY of $CsPbI_3$ PNC could be enhanced (from 53% to 95%).	*Chem. Mater*., 2020, **32**, 6105-6113

IV. Elemental Characterization through ICP-MS

The sample preparation for Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) measurement was carried out by following the modified literature procedure.[3] The as synthesized PNCs were at first purified by centrifuging at 10000 rpm for 20 minutes. The supernatant, which contains unreacted precursor and synthesis by-products, was then discarded. The precipitate was then dispersed in toluene and the solvent was evaporated in rotavapour to get the solid PNC. Then, 10 mg of each PNC samples were dissolved in 10 mL aqua-regia (7.5 mL conc. HCl + 2.5 mL conc. HNO_3) and left for digestion for overnight under rotation. This aqua-regia-digested sample was then diluted 20 times by 2% HNO_3 solution. Finally, diluted digested PNCs were passed through a syringe filter (of pore-size = 0.22 µm)

and the concentrations of the ions were determined using ICP-MS technique in XSeries2 (Thermo Scientific, USA).

Presence of Cs, Pb and Zn in PNC1 and presence of Cs, Pb, Zn as well as Mn in PNC2 have been confirmed through ICP-MS measurement. Relative amount of Zn alloying w.r.t Pb (or Pb+Mn) has also been calculated.

Table S2. Quantitative data of ICP-MS for Zn alloyed $CsPb(Cl/Br)_3$ PNC.

Sample	Mole feed ratio of $PbCl_2$:$ZnBr_2$	Concentration (ppb)			Mole ratio of Cs:Pb:Zn	Mole ratio of Zn/(Zn+Pb)
		Cs	Pb	Zn		
Zn alloyed $CsPb(Cl/Br)_3$	2:1	15.20	33.03	61.57	1:(1.40):(8.26)	0.85

Table S3. Quantitative data of ICP-MS for Mn doped Zn alloyed $CsPb(Cl/Br)_3$ PNC.

Sample	Mole feed ratio of $PbCl_2$:$ZnBr_2$:$MnCl_2$	Concentration (ppb)				Mole ratio of Cs:Pb:Zn:Mn	Mole ratio of Zn / (Zn+Pb+Mn)
		Cs	Pb	Zn	Mn		
Zn alloyed Mn doped $CsPb(Cl/Br)_3$	2:1:4	22.91	39.68	49.99	115.90	1:(1.11):(4.44):(12.26)	0.25

V. Structural Characterization through TEM, PXRD

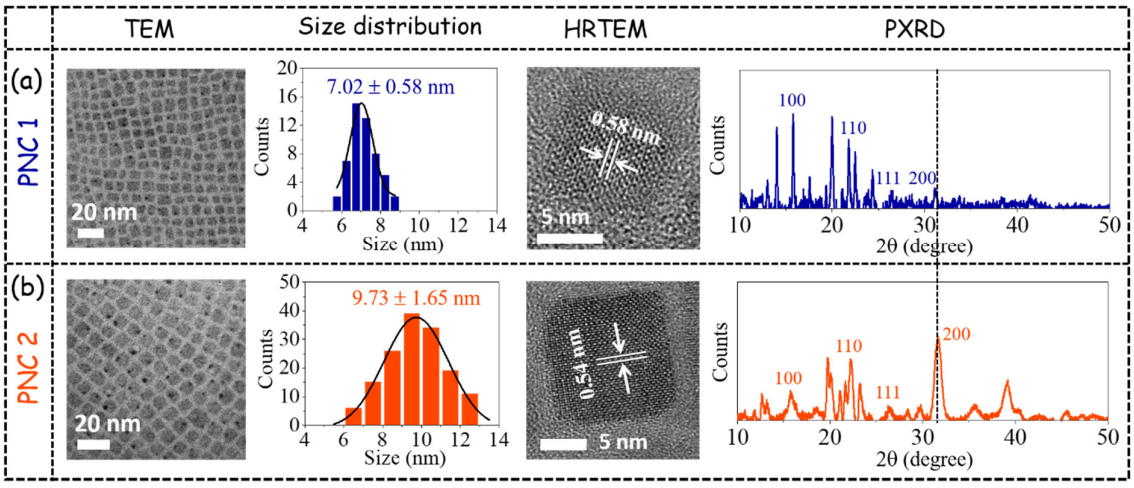

Figure S1. TEM, Size distribution, HRTEM and PXRD pattern of (a) PNC1 and (b) PNC2.

Both the PNCs have been structurally characterized through TEM, HRTEM and PXRD. TEM images confirm that the PNCs are of cubic shape. From the TEM size distribution, the

average size was found to be 7.02 ± 0.58 nm and 9.73 ± 1.65 nm for PNC1 and PNC2 respectively. Similar size has been obtained in previous literature reports.[4-5] Interplanar spacing between (100) planes has been found to be 0.58 nm and 0.54 nm for PNC1 and PNC2, respectively.

VI. Photo-Luminescence Quantum Yield (PLQY) Calculation

The relative PLQY values of Zn alloyed $CsPb(Cl/Br)_3$ PNC and Zn alloyed Mn doped $CsPb(Cl/Br)_3$ PNC have been calculated using the following equation,

$$\phi = \phi_R \frac{OD_R}{OD} \frac{I}{I_R} \frac{n^2}{n_R^2} \quad (3)$$

where ϕ, OD, I and n are the PLQY, optical density, integrated PL intensity and refractive index of the solvent, respectively. Subscript 'R' refers to the reference. For relative PLQY calculation we have used Coumarin 153 dye (PLQY = 58% in ethanol) as reference for all the PNCs.

VII. Mn Doped $CsPb(Cl/Br)_3$ PNC: Comparison with Literature Results

Optical behaviour of our Zn alloyed and Mn doped $CsPb(Cl/Br)_3$ PNC is significantly different from Mn doped $CsPb(Cl/Br)_3$ PNC reported earlier. A comparison table in this regard has been incorporated here.

Table S4. Mn doped $CsPb(Cl/Br)_3$ PNC: comparison with literature results.

Optical properties	Literature report in Mn doped $CsPb(Cl/Br)_3$ PNC	What we have observed in the current Zn alloyed and Mn doped $CsPb(Cl/Br)_3$ PNC
PLQY	PLQY <38% (*Nano Lett*., 2016, **16**, 7376−7380 *J. Mater. Sci*., 2021, **56**, 7494–7507 *RSC Adv*., 2018, **8**, 1940–1947)	PLQY >55%
Temperature dependent PL emission intensity of the host band	PL emission intensity of the host band remains nearly constant upon decreasing the temperature from 290K to 190K (*ACS Energy Lett*., 2019, **4**, 85-93)	PL emission intensity of the host band enhanced by ~5 times upon decreasing the temperature from 290K to 190K
Temperature dependent PL emission intensity of the dopant band	PL emission intensity of the dopant band remains nearly constant upon decreasing the temperature from 300K to 200K (*ACS Energy Lett*., 2019, **4**, 85-93 *J. Phys. Chem. Lett*., 2020, **11**, 2142−2149)	PL emission intensity of the dopant band enhanced by ~5.5 times upon decreasing the temperature from 290K to 190K
	The dopant PL emission intensity decreases as the temperature is decreased from 300K to 190K (*Chem. Mater*., 2017, **29**, 8003-8011 *Chem. Mater*., 2018, **30**, 5346-5352 *J. Luminescence*, 2018, **204**, 10–15)	
Temperature dependent decay of the dopant band	The dopant PL decay dynamics remains nearly constant with decreasing the temperature from 300K to 200K (*ACS Energy Lett*., 2019, **4**, 85-93)	Both the time constants related to the dopant PL decay dynamics increases with decreasing the temperature from 290K to 190K

VIII. Calculations of Radiative and Non-Radiative Decay Rates

The average PL lifetime: $$<\tau> = \frac{A_1\tau_1^2+A_2\tau_2^2+A_3\tau_3^2}{A_1\tau_1+A_2\tau_2+A_3\tau_3} \quad (4)$$

where, τ_i represents time associated with an individual decay component and A_i represents the amplitude associated with that channel.

Radiative lifetime: $$\tau_r = \frac{<\tau>}{PLQY} \quad (5)$$

Radiative decay rate: $$k_r = \frac{1}{\tau_r} \quad (6)$$

Non-radiative lifetime: $$\tau_{nr} = \frac{<\tau>}{1-PLQY} \quad (7)$$

Non-radiative decay rate: $$k_{nr} = \frac{1}{\tau_{nr}} \quad (8)$$

IX. Temperature Dependent Steady State Optical Behaviour

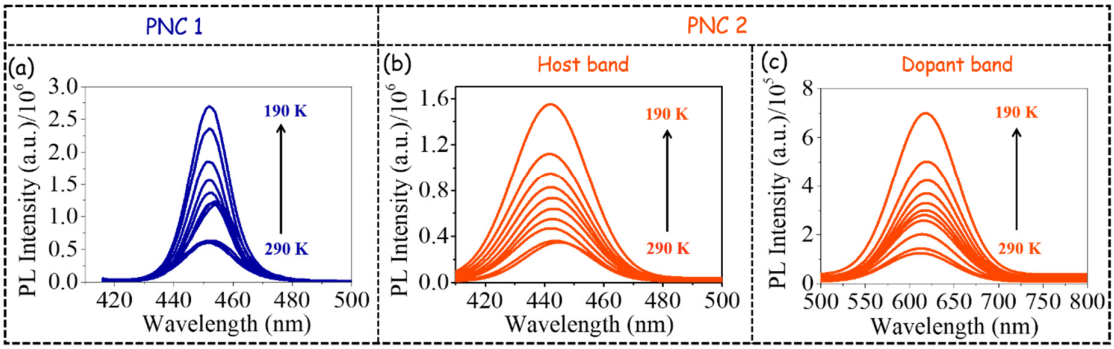

Figure S2. (a) Temperature dependent PL emission of PNC1 and temperature dependent PL emission of (b) host band and (c) dopant band of PNC2.

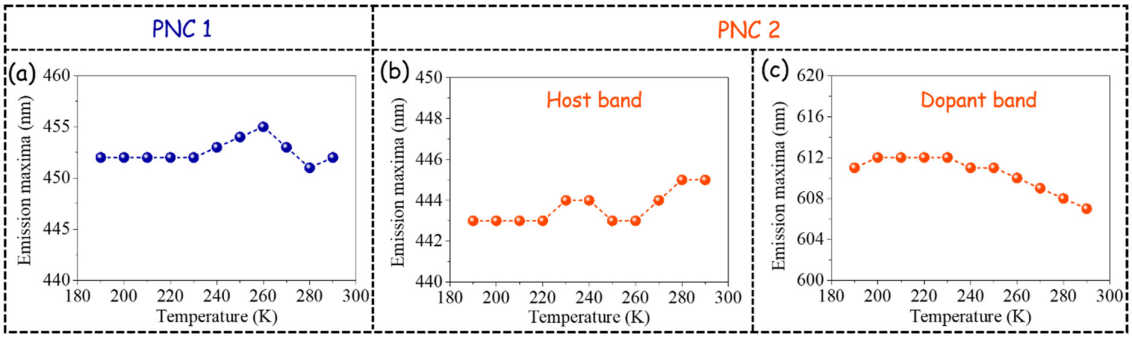

Figure S3. (a) Temperature dependent variation of FWHM of PL emission of PNC1 and temperature dependent variation of FWHM of PL emission of (b) host band and (c) dopant band of PNC2.

X. Calculations of Huang Rhys Factor and Phonon Energy

Huang Rhys factor and phonon energy have been calculated using the following equation,[6]

$$\mathrm{FWHM} = 2.36\sqrt{S}\,\hbar\omega_{\mathrm{phonon}}\sqrt{\mathrm{Coth}\,\frac{\hbar\omega_{\mathrm{phonon}}}{2k_B T}} \qquad (9)$$

Here, S is the Huang Rhys factor and $\hbar\omega_{\mathrm{phonon}}$ is the phonon energy.

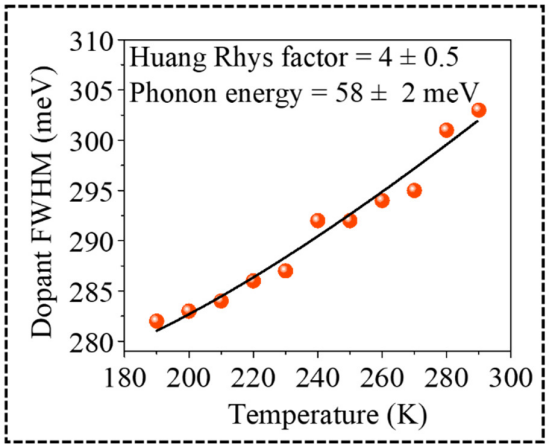

Figure S4. Temperature dependent variation of FWHM of PL emission of dopant band of PNC2.

XI. Temperature Dependent Time Resolved Optical Properties

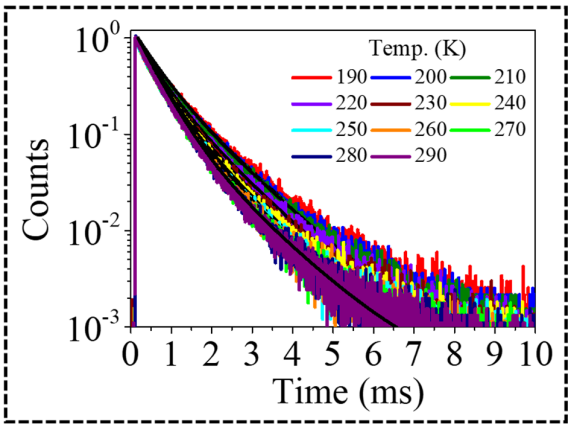

Figure S5. Temperature dependent PL decay of PNC2 (λ_{ex} = 405 nm and λ_{mon} = 601 nm).

Table S5. Temperature dependent PL decay parameters of PNC2 (λ_{ex} = 405 nm and λ_{mon} = 601 nm).

Temperature (K)	τ_1 (µs)	A_1	τ_2 (µs)	A_2	τ_{avg} (µs)	χ^2
190	537.47	0.59	1213.17	0.41	952.61	1.17
200	541.86	0.61	1205.02	0.39	934.54	1.15
210	537.95	0.62	1191.55	0.38	917.47	1.20
220	506.15	0.65	1141.11	0.35	853.33	1.15
230	492.16	0.69	1100.04	0.31	798.67	1.12
240	481.44	0.72	1088.52	0.28	768.63	1.16
250	483.06	0.74	1112.28	0.26	767.56	1.19
260	470.05	0.79	1099.88	0.21	715.21	1.20
270	453.87	0.80	1098.81	0.20	696.62	1.13
280	451.00	0.82	1097.00	0.18	675.86	1.18
290	450.00	0.81	1094.00	0.19	683.88	1.20

XII. Single Particle Spectroscopic Investigations

For the single particle spectroscopic measurement, PNCs were at first embedded in Poly (methyl methacrylate) (PMMA) matrix and spin-coated on a glass coverslip. Then the sample has been probed using our home-built Total Internal Reflection Fluorescence (TIRF) microscope. PNCs were excited with 405 nm CW laser (COHERENT CUBE) through an oil-immersion objective (Zeiss, PlanApo, 100x, NA 1.46). The laser power was maintained <2 mW to avoid bi or multiexciton generation. The PL signal of Zn alloyed $CsPb(Cl/Br)_3$ and Zn alloyed Mn doped $CsPb(Cl/Br)_3$ samples having host emission maximum of ~450 nm has been detected by EMCCD camera with 100 ms integration time and a suitable EM gain. We have taken ~100 single PNCs corrosponding to the host emission and took their corresponding intensity time traces for further analysis. Blinking behaviour of each single host PNCs are analyzed using a home-built code written in MATLAB software. We got a clear bimodal distribution of ON and OFF events for all the PL intensities. Then we put a suitable threshold to separate ON and OFF events which is ~4σ above the peak intensity of lower intensity distribution (where σ indicates the standard deviation of lower intensity distribution (OFF)).[7-11] PL intensity above the threshold is considered to be ON and PL intensity below the threshold 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. From this ON and OFF event duration distributions probability densities of the events as a function of its event duration (ON and OFF event) have been calculated. The ON fraction is calculated as the sum of all single ON-event durations within a certain time trace normalized to the total duration of the same trace (i.e. sum of all single ON and OFF event durations). After plotting the ON and OFF fraction distributions we calculated the peak of ON and OFF fraction through Gaussian fitting. Then we also have plotted the probability density distributions for both ON and OFF events for both the PNCs. We have tried two different equations i.e. inverse power law (IPL) (eq. 10) and truncated inverse power law (TIPL) (eq. 11) to fit both the ON and OFF events. For Zn alloyed $CsPb(Cl/Br)_3$ PNC, both the ON and OFF event probability density distribution were fitted with TIPL equation. For the Zn alloyed Mn doped $CsPb(Cl/Br)_3$ PNC, both the ON and OFF event probability density distributions were fitted with IPL equation.

$$P_{event} = a.t_{event}^{-m} \tag{10}$$

$$P_{event} = a.t_{event}^{-m}.e^{-k.t_{event}} \tag{11}$$

where, *m* is the power law exponent, *k* is the inverse of truncation time (τ_C = 1/k) and *a* is the amplitude.

XIII. References

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