Electronic Supplementary Information

Chemical coupling of halide perovskite nanocrystals with metal quinolate complex for white light generation

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Experimental Section

A. Materials: Lead chloride (PbCl₂), manganese chloride (MnCl₂), cesium carbonate (Cs₂CO₃), 1-octadecene (ODE), oleic acid (OA), oleylamine (OLA), hexane, ethyl acetate, 8-hydroxyquinoline (HQ), sodium hydroxide (NaOH) and calcium chloride (CaCl₂) were purchased and used directly without further purification. Methanol (Merck) and toluene (Merck Emparta for analysis) were purchased and used directly without further purification.

B. Synthesis of HPNCs:^{S1} At first, Cs-oleate solution is prepared by mixing 0.407 g of Cs₂CO₃ with 1.25 ml of OA and 20.0 ml of ODE under constant stirring at 120 °C till the salt was completely dissolved to get a clear solution – which is kept for further use. To a mixture of 0.094 mmol of PbCl₂ and 0.094 mmol of MnCl₂, 0.5 ml of each OA and OLA along with 5 ml of ODE are added and heated at 120 °C under constant stirring until the lead-salt dissolved completely. The reaction temperature is slowly raised to 180 °C and then 0.4 ml of prepared Cs-oleate is injected. The transparent reaction mixture becomes cloudy which indicates the formation of Mn²⁺-doped CsPbCl₃ NCs (i.e. HPNCs). The reaction is arrested within 5 s of Cs-oleate addition by placing the reaction vessel in an ice-water mixture. The crude reaction mixture is subjected to centrifugation at 10000 rpm for 10 min and the supernatant is discarded. The residue is dissolved in 1 ml of hexane and further centrifuged at 6000 rpm for another 5 min. The supernatant is collected and kept for further use.

C. Synthesis of CaQ₂ complex:^{s2} CaQ₂ complex is synthesized by following a previously reported method. 10 mL of 100 mM methanolic solution of 8-hydroxyquinoline is added to 40 mL of 12.5 mM aqueous solution CaCl₂ followed by the addition of 1 mL of 1 M aqueous NaOH solution with vigorous stirring. Then the whole reaction mixture is sonicated for 30 min until the greenish precipitation is observed. Then, the greenish precipitation is filtered through Whatman no. 1 filter paper and wash it with methanol-water mixture thrice to remove unreacted reactant. Finally, the synthesized CaQ₂ is dried in the oven at 40 °C and stored for further experiments.

D. Synthesis of WLE nanocomposite: Four different sets of CaQ₂-HPNCs nanocomposites are prepared by varying the HPNCs: CaQ₂ ratio. In short, 20.0, 30.0, 40.0, and 50.0 μ L of hexane dispersion of CaQ₂ (1 mg / mL) are added to 40.0 μ L of hexane dispersion of HPNCs (with the absorbance of 0.6 at 365 nm) keeping the total volume constant to 100.0 μ L. The same protocol

is followed to prepare nanocomposite with set numbers 1, 2, 3, and 4. It was found that set 3 was the optimum condition for the generation of white light. The solid form of the nanocomposite is prepared followed by drop casting of their individual liquid forms (with set numbers 1, 2, 3, and 4) on a glass slide and dried under vacuum. The emission spectra and corresponding WLE parameters (chromaticity, CRI, and CCT) are measured to confirm the WLE nature of the four sets of solid nanocomposites. The perfect white light is observed for set number 3 – which is further used for testing the luminescence nature including emission, chromaticity, CRI, CCT photoluminescence quantum yield (PLQY), photostability, and timedependent stability of WLE nanocomposite.

E. Characterizations, Analysis & Instruments:

(i) Thin-film XRD analysis: A Rigaku TTRAX-III X-ray diffractometer, running with a Cu K α source $(\lambda = 1.54 \text{ Å})$, is used to record XRD spectra of the Mn²⁺-doped CsPbCl₃ perovskite NCs before and after the interaction with CaQ_2 complex (broadcasted in glass slides separately).

(ii) Transmission electron microscopic (TEM) and energy dispersive X-ray (EDX) analysis: TEM, HRTEM images, and EDX analysis of the samples are captured by using JEOL JEM 2100F (maximum accelerating voltage: 200 kV) and analyzed by Gatan Digital Micrograph software.

(iii) X-ray Photoelectron spectroscopic (XPS) analysis: XPS spectra of the samples are recorded by using a Physical electronics, USA-made X-ray photoelectron spectrophotometer (Model: PHI 5000 Versa Probe III with X-ray source monochromated K alpha 1486.7 eV).

(iv) Fourier transform infrared spectroscopy.^{S2-S3} FTIR spectra of the Mn²⁺-doped CsPbCl₃ perovskite NCs before and after the interaction with CaQ₂ complex and only CaQ₂ complex are recorded by using a Perkin-Elmer spectrophotometer (Model: Spectrum Two, with ATR).

(v) UV & PL measurements: PerkinElmer Lambda 35 UV-vis spectrophotometer and HORIBA Jobin Yvon FluoroMax-4 spectrofluorimeter are used to record all absorption and photoluminescence spectra of the samples, respectively.

(vi) Capturing digital photos: All digital photographs are taken under the excitation from a spectrofluorimeter as a source and using Realme 5 mobile with default settings.

(vii) Chromaticity and CCT analysis: OSRAM color calculator (CIE-1931) software is used to calculate the chromaticity, CRI, and CCT from the photoluminescence spectra.

(viii) Stability measurements: Photostability of the solid WLE nanocomposite is tested by calculating corresponding photoluminescence intensity at respective emission maxima (i.e. 585, 464, and 405 nm) under constant photo irradiation of 365 nm light for 10 minutes inside a HORIBA Jobin Yvon FluoroMax-4 spectrofluorimeter instrument. The luminescence stability of the WLE nanocomposite is tested for 7 days.

(ix) PLQY analysis: PLQY of the WLE composite is calculated using an earlier reported method.⁵⁴ HORIBA Jobin Yvon FluoroMax-4 spectrofluorimeter is used to record photoluminescence spectra of the materials and the blank. The following equation is used to calculate PLQY.

Emission_(sample) – Emission_(blank)

 $PLQY = \frac{PLQY}{Absorbance_{(blank)} - Absorbance_{(blank)}}$

where "Emission" is the area under the emission curve within the emission range and absorbance is the area under the emission curve within the excitation range



Fig. S1. X-ray photoelectron spectra (XPS) with respect to **(A)** 3d peaks of Cs⁺, **(B)** 4f peaks of Pb²⁺, and **(C)** 2p peaks of Mn²⁺ of (i) HPNCs and (ii) CaQ₂-HPNCs. **(D)** 2p peaks of Ca²⁺ of CaQ₂-HPNCs. Further, the presence of 2p peaks of Ca²⁺ ions in the XPS of the nanocomposite clearly describes the successful coupling of the CaQ₂ complex with HPNCs. The peak intensity of Mn²⁺ is relatively weak compared to other elements (such as Cs, Pb, and Cl), possibly due to the lower amount of dopant in HPNCs. No obvious peak is observed for Mn $2p_{1/2}$ - which is well matched with earlier reports.^{S5-S6}



Fig. S2. (A) Digital photograph (λ_{ex} = 365 nm), **(B)** emission spectrum (λ_{ex} = 365 nm), and **(C)** corresponding color chromaticity coordinates of solid CaQ₂ complex. **(D)** UV-vis spectra of CaQ₂- complex (in chloroform).

Table S1. Tabulated peaks (or functional groups) and corresponding vibrational frequencies obtained from FTIR spectral data as shown in Fig. 1D, Manuscript.^{S2-S3}

Vibrational Frequency (Cm ⁻¹)	Functional groups of CaQ ₂ complex ^{S2-S3}	HPNCs	CaQ ₂ - HPNCs
485, 551	Ring deformation	Absent	Present
595, 648	C-H in-plane deformation (HQ)	Absent	Present
790	C-H wagging	Absent	Present
742	C-H in and out plane deformation(HQ)	Absent	Present
805, 823	C-H out plane deformation (HQ)	Absent	Present
1035, 1070, 1309, 1362, 1417	HQ-molecule stretching, Ring deformation	Absent	Present
1103	-C-O-M	Absent	Present
1226, 1271	C-H stretching		
1454	phenyl group (HQ)	Absent	Present
1498	pyridyl group (HQ)	Absent	Present
1568 <i>,</i> 1600	C-C/C-N stretching (HQ)	Absent	Present

Table S2. Tabulated average optical data (obtained from Fig. 2C-2D, Manuscript and Fig. S2, ESI) comparison of solid (i) HPNCs, (ii) CaQ₂ complex, and (iii) CaQ₂-HPNCs.

Materials	λ_{em} (nm)	Chromaticity (x, y)	CRI	CCT (K)
HPNCs	405 <i>,</i> 585	(0.47, 0.42)	41	2565
CaQ ₂ complex	464	(0.18, 0.22)	-	950000
CaQ ₂ -HPNCs	405,464,585	(0.33, 0.32)	80	5483



Fig. S3. (A) Emission spectra (λ_{ex} = 365 nm), **(B)** corresponding color chromaticity coordinates in CIE diagram of CaQ₂ complex coupled HPNCs obtained from their 4 sets of mixtures of CaQ₂ and HPNCs. The individual spectrum was recorded after drying each sample at room temperature. The experiments were performed in triplicate. Set-3 is used for further spectroscopic analysis.

Table S3. Tabulated data (extracted from Fig. S3, ESI) of chromaticity, CRI, and CCT of CaQ_2 complex coupled HPNCs obtained from their 4 sets of mixtures of CaQ_2 and HPNCs. The individual spectrum was recorded after drying each sample at room temperature. The experiments were performed in triplicate. Set-3 is used for further spectroscopic analysis.

Set	Chromaticity (x, y)	CRI	CCT (K)
1	(0.3953±0.0064, 0.3624±0.0045)	62.33 ±1.53	3490.33 ±123.57
2	(0.3699±0.0062, 0.3437±0.0044)	69.33 ±1.53	4058.33±174.32
3	(0.3326±0.0036, 0.3176±0.0016)	80.00±1.00	5483.33 ±192.18
4	(0.2942±0.0014, 0.2992±0.0010)	86.00±0.00	8231.33±145.34

Table S4. Tabulated data (extracted from Fig. 2G-2H, Manuscript) of chromaticity, and CCT of the solid form of CaQ₂-HPNCs at the time interval of 7 days.

Time	Chromaticity (x, y)	CRI	CCT (K)
0 day	(0.33, 0.32)	80	5483
7 days	(0.33, 0.31)	82	5893



Fig. S4. Comparison of emission spectra (λ_{ex} =365 nm) of blank and WLE nanocomposite for the measurement of PLQY (range 300-700 nm).

Table S5. PLQY data (obtained from Fig. S4, ESI) of WLE nanocomposite.

Bla	nk	WLE Samp	ole + Blank	ΡΙΟΥ
Absorbance	Emission	Absorbance	Emission	
10524969	7614032	3941455	11176776	0.541

Table S6. Comparison of WLE properties of the presented WLE nanocomposite with earlier reported MHP-based WLE materials.

SI No	White Light Emitting Properties			
51. NO.	CIE (x,y)	CCT (K)	CRI	
This Work	(0.33, 0.32)	5483	80	
Ref. S7	(0.28, 0.36)	7863	73	
Ref. S8	(0.37,0.42)	4426	84	
Ref. S9	(0.33 <i>,</i> 0.36)	5500	78	
Ref. S10	(0.30, 0.49)	Not Reported	27.5	
Ref. S11	(0.33, 0.29)	19000-4250	Not Reported	
Ref. S12	(0.337, 0.320)	6507	95	
Ref. S13	(0.321, 0.334)	6071	78	
Ref. S14	(0.41, 0.43)	3836	91	
Ref. S15	(0.41, 0.38)	3209	88	
Ref. S16	(0.333, 0.341)	5469	98	
Ref. S17	(0.346,0.378)	5049	94	
Ref. S18	(0.351, 0.346)	4743	Not Reported	
Bright Mid-day Sunlight	(0.33, 0.33)	5000-6000	75	

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