Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Precursor Non-stoichiometry to Enable Improved $CH_3NH_3PbBr_3$ Nanocrystal LED Performance

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Small-Angle X-ray Scattering

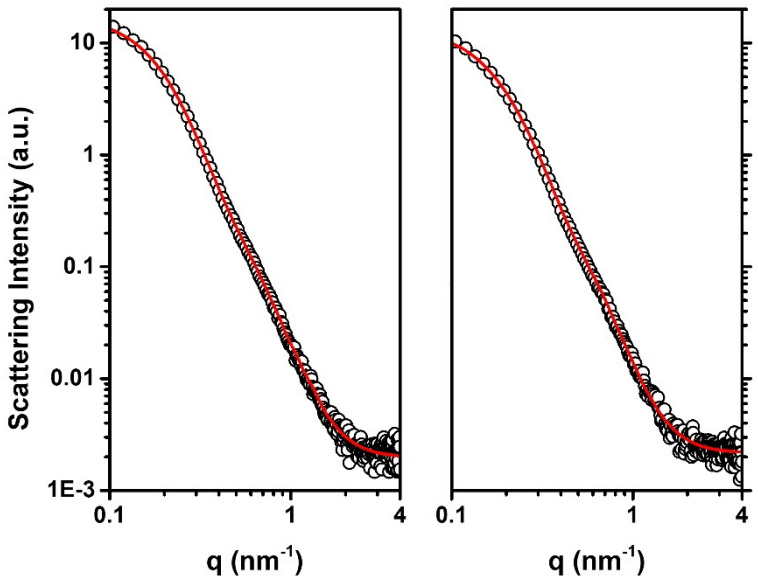

Figure S1. Exemplary fits for the scattering curves obtained from the small angle X-ray scattering (SAXS) measurements for CH_3NH_3Br:$PbBr_2$ ratios of 1:1 (left) and 1.15:1 (right).

X-ray Photoelectron Spectroscopy

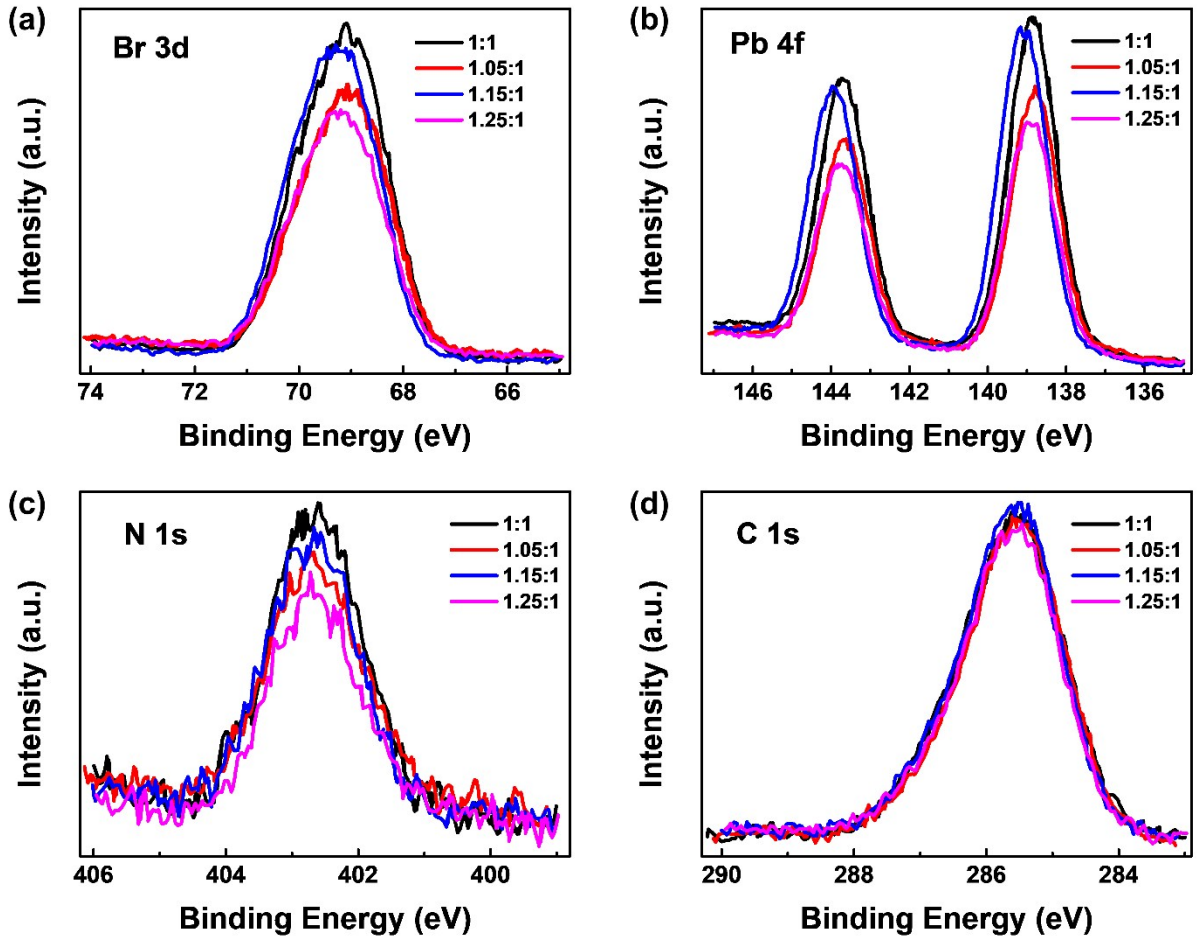

Figure S2. XPS (a) Br 3d spectra, (b) Pb 4f spectra, (c) N 1s spectra, and (d) C 1s spectra of the NCs prepared by varying the CH_3NH_3Br:$PbBr_2$ ratios viz. 1:1 (black), 1.05:1 (red), 1.15:1 (blue) and 1.25:1 (magenta).

Table S1. Elemental composition of the NCs synthesized from 1:1, 1.05:1, 1.15:1 and 1.25:1 ratios of CH_3NH_3Br:$PbBr_2$ extracted from X-ray photoelectron spectroscopy measurement.

MABr:$PbBr_2$	**1:1**	**1.05:1**	**1.15:1**	**1.25:1**
Br/Pb	2.64	2.67	2.56	2.69
N/Pb	1.26	1.33	1.09	1.23
C/Pb	1.03	1.04	1.30	1.60

Analysis of XPS spectra revealed a Br deficiency for all the NCs, which was more pronounced for 1.15:1 (Table S1). All the NCs also exhibited excess N on the NC surface, however, the Pb:N ratio was closest to 1 for the 1.15:1 precursor ratio. In addition, the Pb 4f binding energy spectra displayed a minor blue shift of 0.2 eV for the 1.15:1 compared to the other ratios (Figure S2). These results point to possible differences in the ligand binding on the NC surface for the different precursor ratios. However, further studies are required to elucidate the exact ligand binding mechanisms. Nuclear magnetic resonance (NMR) measurements could be performed on the NC inks as well as the colloidal solutions at various stages of NC synthesis to reveal the nature of ligands attached to the NC surface. Additionally, temperature-dependent spectroscopic studies may help clarify the binding energies at the ligand-NC interface.

Reaction Yield

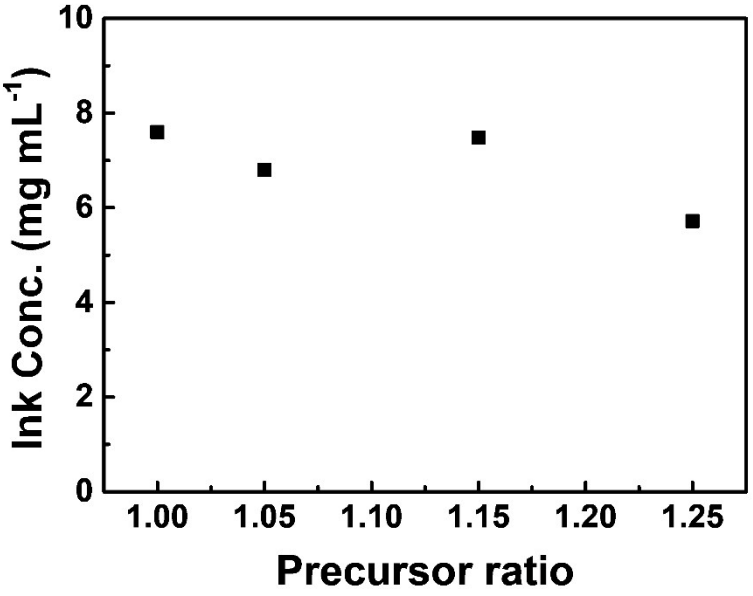

Figure S3. NC ink concentration/ NC synthesis yield for the NCs prepared from the various $CH_3NH_3Br:PbBr_2$ ratios viz., 1:1, 1.05:1, 1.15:1, and 1.25:1.

Table S2. Steady state PL peak positions and full width half maximum (FWHM) obtained from the non-linear pseudo-Voigt curve fits.

Ratios	PL peak wavelength (nm)	FWHM (nm)
1:1	522.7	22.2
1.05:1	523.7	22.1
1.15:1	523.6	22.1
1.25:1	521.7	22.3

Scanning Electron Microscopy

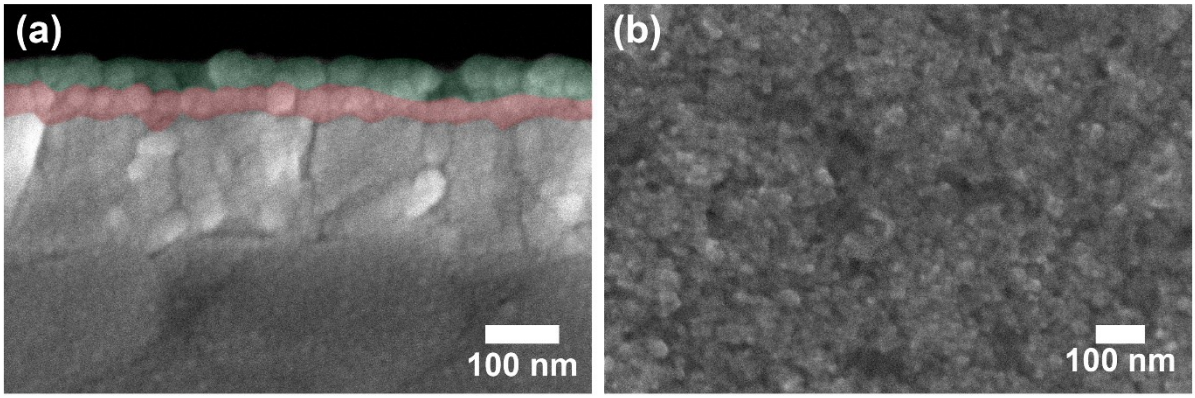

Figure S4. Scanning electron microscopy (SEM) images of (a) cross section and (b) top morphology of NC ink prepared from 1.15:1 ratio of CH_3NH_3Br:$PbBr_2$, spin coated on top of ITO/PEDOT:PSS. The green and red layers in (a) represent the perovskite emitter and PEDOT:PSS layer, respectively.

Band Diagram and Photoelectron Spectroscopy in Air

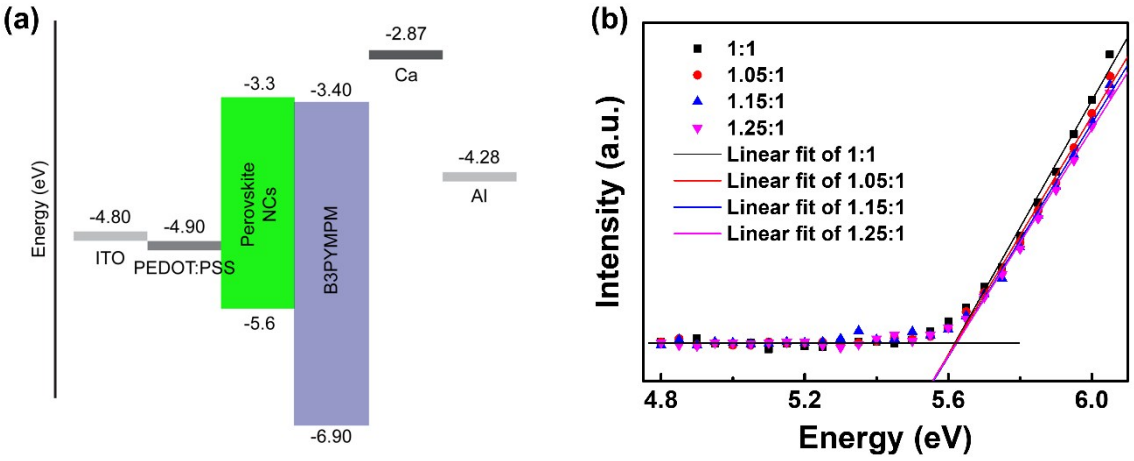

Figure S5. (a) Schematic diagram of the flat band energy levels of the LED device stack. (b) Valence band maxima (VBM) of the various NC inks prepared from the $CH_3NH_3Br:PbBr_2$ ratios of 1:1 (black), 1.05:1 (red), 1.15:1 (blue), and 1.25:1 (magenta), calculated from the photoelectron spectroscopy in air (PESA) measurements.

Device Performance

Table S3. Comparison of our 1.15:1 precursor ratio $CH_3NH_3PbBr_3$ NC LED with other $CH_3NH_3PbBr_3$ NC-based LEDs reported in literature.

Morphology	**Device Architecture**	**V_T (V)**	**Max CE (cd A^{-1})**	**Max PE (lm W^{-1})**	**EQE (%)**	**L_{max} (cd m^{-2})**	**Publication (Month/Year)**
NP (amorphous)	ITO/PEDOT:PSS/Pe/ TPBi/Cs_2CO_3/Al	3.1	11.49	7.84	3.8	3515	Jun 2016[1]
NC	**ITO/PEDOT:PSS/Pe/ B3PYMPM/Ca/Al**	**2.7**	**6.45**	**5.98**	**1.75**	**2721**	**This work**
NC	ITO/PEDOT:PSS/Pe/ TPBi/CsF/Al	2.9	4.5	3.5	1.1	2503	Dec 2015[2]
Nanoplatelet	ITO/PEDOT:PSS/Pe/ PVK:PBD/BCP/LiF/Al	3.8	n.r.	1.0	0.48	10590	Nov 2015[3]

V_T is turn-on voltage, CE is current efficiency, PE is power efficiency, EQE is external quantum efficiency, L_{max} is maximum luminance, Pe refers to the perovskite emitter, viz. $CH_3NH_3PbBr_3$, n.r. indicates the value is not reported. PEDOT:PSS = poly(3,4-ethylenedioxythiophene):polystyrene sulfonate ;TPBI = 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole); B3PYMPM = 4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine; PVK:PBD = (poly(9-vinylcarbazole):2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole); and BCP = bathocuproine

References

1. J. Xing, F. Yan, Y. Zhao, S. Chen, H. Yu, Q. Zhang, R. Zeng, H. V. Demir, X. Sun, A. Huan and Q. Xiong, *ACS Nano*, 2016, **10**, 6623-6630.
2. H. Huang, F. Zhao, L. Liu, F. Zhang, X.-g. Wu, L. Shi, B. Zou, Q. Pei and H. Zhong, *ACS Applied Materials & Interfaces*, 2015, **7**, 28128-28133.
3. Y. Ling, Z. Yuan, Y. Tian, X. Wang, J. C. Wang, Y. Xin, K. Hanson, B. Ma and H. Gao, *Advanced Materials*, 2016, **28**, 305-311.