Phase transferred and Non-coated, Water Soluble Perovskite Quantum Dots for Biocompatibility and Sensing

Sanjayan C. G and R Geetha Balakrishna*

Centre for Nano and Material Sciences, Jain (Deemed-to-be University), Bangalore 562112, Karnataka, India

*Author for Correspondence: br.geetha@jainuniversity.ac.in

---

1. Experimental Section.

1.1. Materials Required

Required chemicals such as cesium carbonate (Cs_2Co_3) (99%), lead bromide ($PbBr_3$) (99.99%), oleic acid (OA) (≥99%), oleyl amine (OAm) (70%), octadecane (ODE) (90%), succinic acid (SA) (≥90%), toluene (99.8%), ethyl acetate (99.8%) and Histamine, Dopamine HCl, Thiamine HCl were procured from Sigma Aldrich. phosphate buffer saline (PBS) tablets were purchased from Himedia. Double distilled water was used throughout wherever necessary.

1.2. Synthesis of $CsPbBr_3$ PQDs

$CsPbBr_3$ perovskite QDs were synthesized by hot-injection method as reported in our previous publication[1]. The synthesized $CsPbBr_3$ PQDs will know as OA PQDs.

1.3. Synthesis of Aqueous $CsPbBr_3$ PQDs

Aqueous $CsPbBr_3$ PQDs was synthesized by our previous protocol[2]. Succinic acid (SA, 100 mg) was dissolved in 5 ml of 0.1M PBS buffer (pH 7) to obtain SA-PBS solution. 1:1 ratio of OA PQDs and SA PBS was allowed to react for 30 minutes, after 30 mins of vertexing, transfer of PQDs from toluene to water was observed. The transfer of PQDs clearly indicates the formation of Aqueous(A) $CsPbBr_3$ PQDs (APQDs). The obtained APQDs were centrifuged and washed with water and the final pellet was dispersed in PBS for further characterization studies.

1.4. Sensing protocol of Analytes

For sensing bioamines in water, the mentioned bioamines are dissolved in water and the stock concertation of the histamine, thiamine HCL, Hexamethylenediamine, Phenethylamine and

dopamine HCL are maintained at 90 µM, 104.4 µM, 107.5 µM, 103.1 µM and 94.87 µM from which 1 µL of analyte was added to 1ml of APQDs solution in intervals for recording changes in PL during sensing. 0.6 µM of APQDS in 1 mL of water was used as a fluorescent probe.

2. Instrumentation.

Shimadzu UV 1800 PC spectrophotometer and Shimadzu RF 301 PC Spectro fluorophotometer were used to characterize the optical spectroscopy studies, and the TALOS F200S G2 200 KV, FEG, CMOS camera 4K x 4K Transmission Electron Microscope (TEM) was used to examine the material's structural morphology. The needed sample was prepared for TEM by drop casting it onto copper grids, where it was then thoroughly dried and kept in vacuum. Brucker Alpha II ATR-IR spectrometer was used to evaluate the surface's functional group. Structural and crystalline natures of developed PQDs were analyzed by drop casting $CsPbBr_3$ PQDs and ligand exchanged $CsPbBr_3$ PQDs on glass slides and dried under vacuum condition and analyzed by X-Ray Diffractometer (XRD) respectively.

3. Williamson-hall's plots

The lattice strain of OA PQDs and APQDs was calculated by the Williamson Hall's plot which shows the increase in lattice strain from 1.31×10^{-4} (OA PQDs) to 3.2×10^{-4} (APQDs) after phase transfer. The exchange of surface ligands on OA PQDs with short chain SA ligand allows the formation of solvated carboxylic dimer connecting PQDs and this causes increase in the lattice strain on APQDs, leading to reduction in crystallite size as well as particle size as explained in the section 3.1.

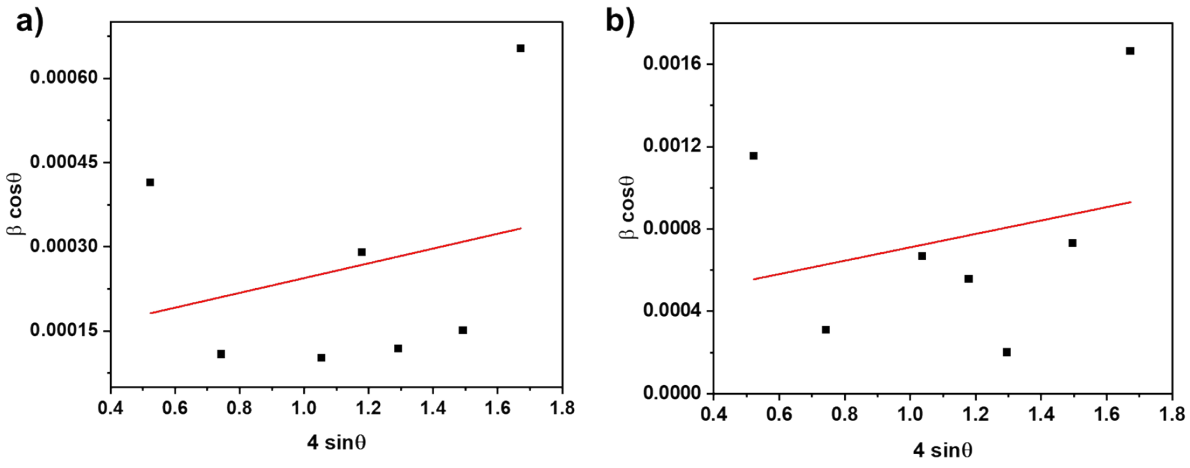

Figure S1. Williamson -Hall's plots of (a) OA PQDs and (b) APQDs

Si. No	Quantum Dots	Quantum Yield (%)	Ref
1	$CuInS_2/ZnS$	38	[3]
2	CdTe	56.68	[4]
3	InP/ZnS	67	[5]
4	ZnSe/ZnS	70.6	[6]
5	CdSe	76.57	[7]
6	ZnSe/CdS/ZnS	82	[8]
7	ZnSe/ZnS:Mn/ZnS	84	[9]
8	CQDs	85	[10]
9	Aqueous Perovskite quantum dots	87	Present work

Table ST1. Comparison of QYs of APQDS with various other quantum dots reported previously.

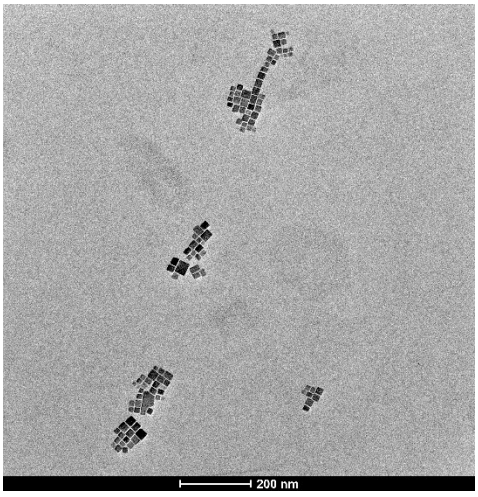

Figure S2. Wide view of TEM image of APQDs

4. IR studies

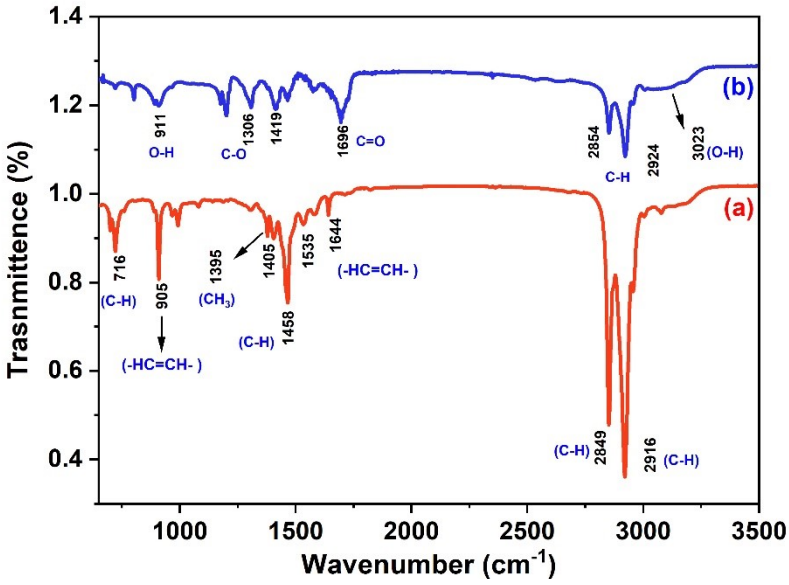

Figure S3. IR spectra of a) OA PQDs in toluene b) APQDs in water.

5. XRD studies

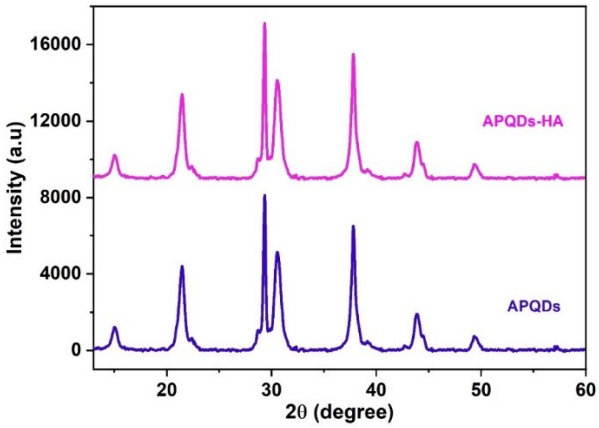

Figure S4. XRD patterns of APQDs and APQDs-HA.

6. Determination of dissociation constant-K_d

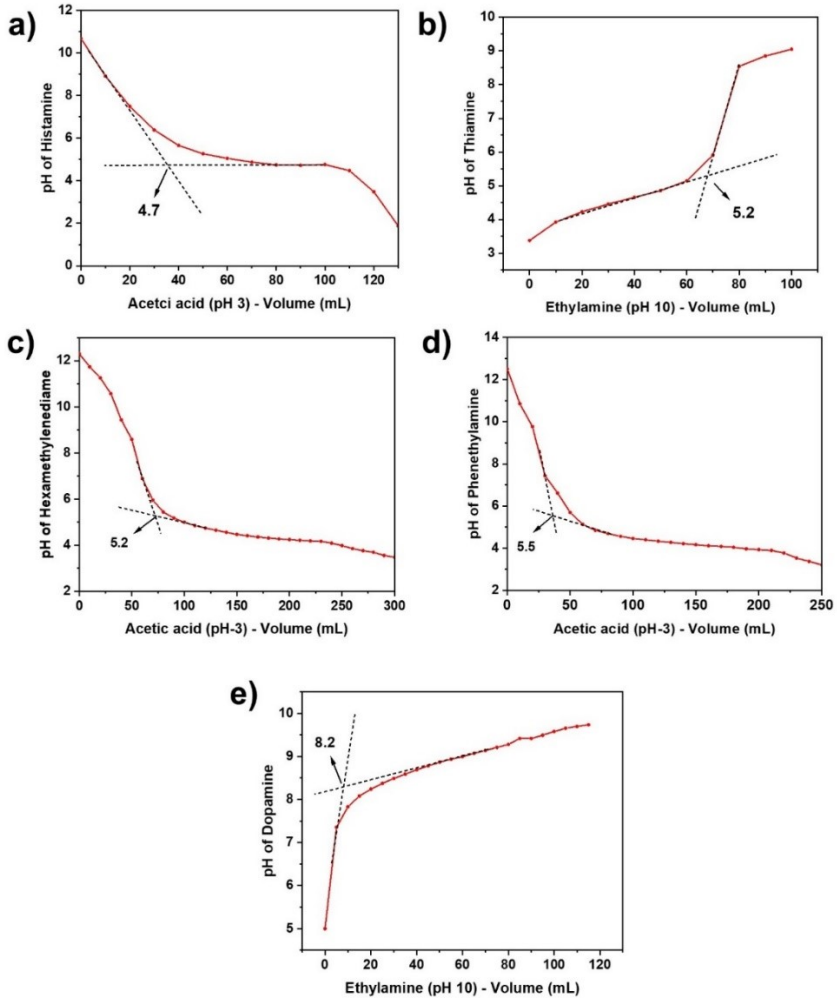

Figure S5. Titration curve for of bioamines to find the equivalence point a) HA b) TA c) HMA d) PEA e) DA.

Sample	PL intensity	Obtained Concentration (µM)	Spiked concentration (µM)
Probe	435	0	0
Sample 1	414	0.375	0.4
Sample 2	356	0.829	0.8
Sample 3	296	1.265	1.3

Table ST2. Real time analysis performed for spiked samples of histamine.

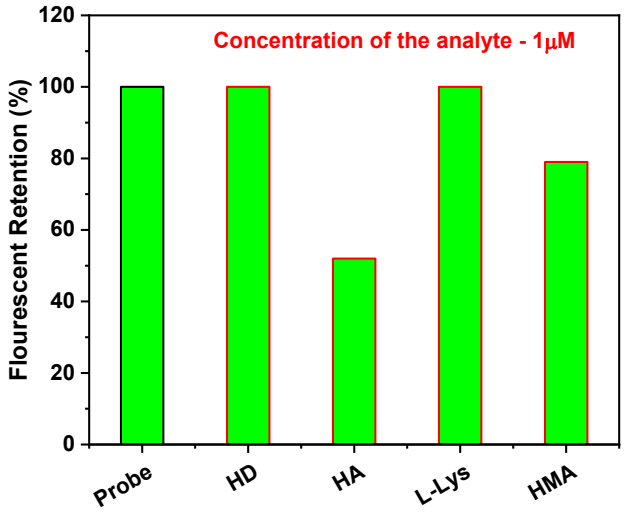

Figure S6. Bar graph of change in PL intensity of the probe for amino acids Histidine (HD), L-Lysine (L-LYS) and its decarboxylated form Histamine (HA), Hexamethylenediamine (HMA).

References:

1. V. V. Halali, R. Shwetha Rani, R. Geetha Balakrishna and S. Budagumpi, *Microchemical Journal*, 2020, **156**, 104808.
2. S. C G, J. Mannekote Shivanna, J. D. Schiffman, S. Mohan, S. Budagumpi and R. G. Balakrishna, *ACS Applied Materials & Interfaces*, 2022, **14**, 38471-38482.
3. Y. s. Kim, Y. Lee, Y. Kim, D. Kim, H. S. Choi, J. C. Park, Y. S. Nam and D. Y. Jeon, *RSC Advances*, 2017, **7**, 10675-10682.
4. M. Shen, W. Jia, Y. You, Y. Hu, F. Li, S. Tian, J. Li, Y. Jin and D. Han, *Nanoscale Research Letters*, 2013, **8**, 253.
5. T. Watanabe, Y. Iso, T. Isobe and H. Sasaki, *RSC Adv*, 2018, **8**, 25526-25533.
6. C. Shu, B. Huang, X. Chen, Y. Wang, X. Li, L. Ding and W. Zhong, *Spectrochim Acta A Mol Biomol Spectrosc*, 2013, **104**, 143-149.
7. B. Gao, C. Shen, S. Yuan, Y. Yang and G. Chen, *Journal of Nanomaterials*, 2013, **2013**, 1-7.
8. S. Wang, J. J. Li, Y. Lv, R. Wu, M. Xing, H. Shen, H. Wang, L. S. Li and X. Chen, *Nanoscale Res Lett*, 2017, **12**, 380.
9. H. Nishimura, T. Maekawa, K. Enomoto, N. Shigekawa, T. Takagi, S. Sobue, S. Kawai and D. Kim, *Journal of Materials Chemistry C*, 2021, **9**, 693-701.
10. H. Lin, J. Huang and L. Ding, *Journal of Nanomaterials*, 2019, **2019**, 1-9.