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Bidentate Ligand-passivated CsPbI₃ Perovskite Nanocrystals for Stable Near-unity Photoluminescence Quantum Yield and Efficient Red Light-emitting Diodes

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Supporting Information Placeholder

ABSTRACT: Although halide perovskite nanocrystals (NCs) are promising materials for optoelectronic devices, they suffer severely from chemical and phase instabilities. Moreover, the common capping ligands like oleic acid and oleylamine that encapsulate the NCs will form an insulating layer, precluding their utility in optoelectronic devices. To overcome these limitations, we develop a post-synthesis passivation process for CsPbI₃ NCs by using a bidentate ligand, namely 2,2'-Iminodibenzoic acid. Our passivated NCs exhibit narrow red photoluminescence with exceptional quantum yield (close to unity) and substantially improved stability. The passivated NCs enabled us to realize red light-emitting diodes (LEDs) with 5.02% external quantum efficiency and 748 cd/m² luminance, surpassing by far LEDs made from the non-passivated NCs.

The development of solution-processed halide perovskites has disrupted the global roadmap of semiconductors.¹⁻⁴ While research on halide perovskites was solely motivated by solar cell technologies, it has quickly grown to encompass the whole optoelectronic research community.⁵ The use of all-inorganic cesium lead halide perovskite (CsPbX₃, X = Cl, Br, and I) nanocrystals (NCs) exhibiting high photoluminescence quantum yields (PLQY), narrow emission,⁶ and tunable absorption/emission wavelengths⁷ has accelerated the emergence and development of perovskite-based nanomaterials for applications such as light-emitting diodes (LED),⁸⁻¹⁰ solar cells,¹¹ lasers,¹² photodetectors,¹³ and visible-light communication.¹⁴

Since the first reported synthesis of nearly monodispersed CsPbX₃ NCs using a hot-injection approach,¹⁵ many efforts have been expended on optimizing NC synthesis procedures to facilitate the fabrication of

LEDs.⁸⁻¹⁰ Despite significant advancements in the development of LEDs based on perovskite NCs,¹⁶⁻¹⁸ especially for green LEDs for which external quantum efficiencies (EQE) have exceeded 10%,¹⁹ device performances are still far from meeting application requirements, particularly when red LEDs are needed. A common issue is the intrinsic chemical instability of CsPbX₃ NCs due to the dynamic nature of the bonding between the inorganic surface and the long-chain capping ligands.²³⁻²⁶ Furthermore, common capping ligands like oleylamine (OAm) and oleic acid (OA) act as electrically insulating layers on the NC's surface which hinder significantly charge carrier injection and transport at the interface of the ensuing device. To add to this list of challenges afflicting perovskites, CsPbI₃ NCs in particular suffer from a non-perovskite phase transition at room temperature.²⁷ While recent efforts have led to considerable stabilization of iodide perovskite NCs,^{11, 28-29} there is still a critical need for a NC passivation strategy that combines stability and high PLQY with surface ligands that are compatible with the charge transport requirements of LEDs and optoelectronic applications in general.³⁰

In this communication, we explore a bidentate ligand, namely 2,2'-Iminodibenzoic acid (IDA, Figure 1a), to passivate the NC surface. Theoretical calculations (*vide infra*) show much stronger bonding between the perovskite surface and this ligand in comparison to OA. The IDA-treated NCs display a PLQY of over 95% (much higher than untreated NCs), significantly enhanced stability in the desired cubic perovskite phase, as well as enhanced electronic coupling between ligands and NCs. As a result, we were able to fabricate red LEDs with broadly superior characteristics (i.e., two-

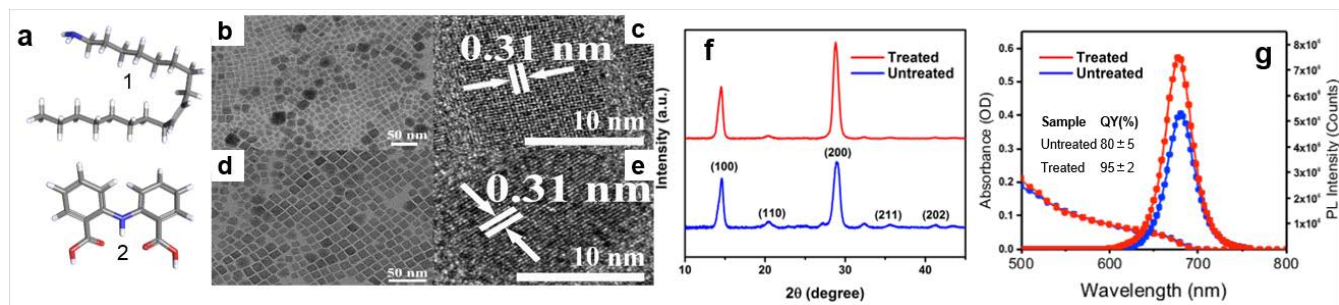


Figure 1. a) Molecular structure of OA (1), and IDA (2) ligands. b) Low- and high- e) magnification TEM images of untreated QDs. d) Low- and high- e) magnification SEM images for IDA-treated NCs. (f) Powder XRD patterns of untreated (blue) and IDA-treated NCs (red). (g) Absorption and PL spectra for untreated (blue) and IDA-treated NCs (red) from equimolar concentrated solutions, with the relative PL quantum yield in the inset.

fold higher EQE and luminescence intensity) to those of LEDs based on pristine NCs.

CsPbI₃ perovskite NCs were synthesized following a well-established synthesis process with minor modifications^{11, 31} (see SI for details). The purified NCs (labelled as “untreated” NCs) had a cubic shape with an average dimension of 13.6±2.9 nm (Figure S1a) determined by high-resolution transmission electron microscopy (HR-TEM) (Figure 1b). Passivated NCs were obtained by adding a small amount of IDA powder directly into a solution of untreated NCs (see SI for details). After treatment, the excess IDA was removed by centrifugation. The IDA-treated NCs were cubic shaped (Figure 1d) with an average size of 12±1.5 nm (Figure S1b). It should be noted that the particles are easily aggregated if IDA is used directly in the synthesis (Figure S2). Both the untreated and treated NCs have a lattice distance of 0.31 nm, corresponding to the (200) crystal plane of the cubic phase perovskite (Figure 1c and 1e), suggesting that the crystal structure remained unchanged during treatment process, which was further confirmed by X-ray diffraction (XRD, Figure 1f).

However, significant changes in optical properties were observed. With IDA treatment, PLQY increased to near unity (95±2%) compared with that of the untreated NCs (80±5%). Accompanying the rise in PLQY, PL emission retained the same peak position at 680 nm, while no significant change was observed in the absorption spectrum (Figure 1g). Moreover, the PL lifetime exhibited a slight improvement from 10.5 ns to 12.8 ns after IDA treatment (Figure S3), suggesting that a reduction in surface trap states occurred through IDA pas-

sivation.^{32,33}

To investigate how IDA affects the NC surface, we performed X-ray photoelectron spectroscopy (XPS), solution ¹H nuclear magnetic resonance (¹H-NMR), and infrared spectroscopy (IR) experiments on untreated and treated NCs. The XPS analysis revealed no significant changes in the Cs 3*d*, Pb 4*f*, I 3*d* core-level spectra of both samples (Figure S14); yet, the high-resolution spectra of the N 1*s* core-level exhibited a noticeable variation (Figure S15). We fitted the N 1*s* core level for untreated NCs to a single peak at 401.8 eV, corresponding to protonated amine groups (NH₃⁺) from oleyl ammonium. An additional peak at 399.4 eV appeared in the IDA-treated NC N 1*s* core-level spectrum, attributed to -NH- group from IDA.³⁴⁻³⁵ Indeed, the ratio of the two different N 1*s* core levels (NH₃⁺ and -NH-) by comparing the integrated area of the two peaks suggests that the OAm to IDA ratio in the passivated NCs was 3.3:1. The existence of the -NH- group after IDA treatment was further verified by ¹H-NMR with a signal at 10.9 ppm, while the proton signal of the -COOH group from IDA at 13 ppm disappeared. This suggests that the -COOH functional groups in IDA were converted to carboxyls (Figure S6). Quantitative NMR analysis also reveals a significant reduction in OA after IDA treatment (Figure S7 and Table S1). We also investigated the binding mode of IDA on the NCs by IR spectroscopy. Four additional IR peaks are recorded for IDA treated NCs. The peaks at 1602 cm⁻¹ and 1496 cm⁻¹ are ascribed to aromatic C=C vibration, while 1575 cm⁻¹ is ascribed to the conjugated aromatic ring and 750 cm⁻¹ is ascribed to aromatic C-H bending, respectively³⁶ (Figure S8). Thus, we conclude

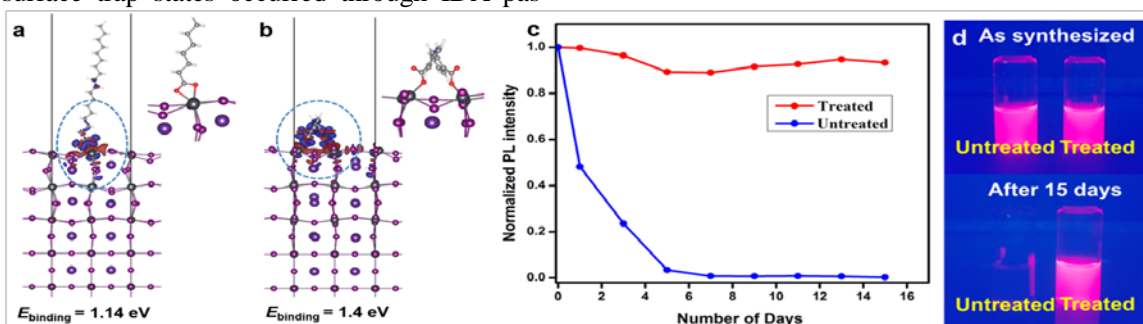


Figure 2. a), b) Surface charge redistributions of optimized PbI₂-rich CsPbI₃ surfaces with OA and IDA ligand modification. c) Normalized PLQY intensities as a function of days for untreated (blue) and IDA-treated NCs (red). d) Photograph of untreated and treated QDs as-synthesized and aged for 15 days.

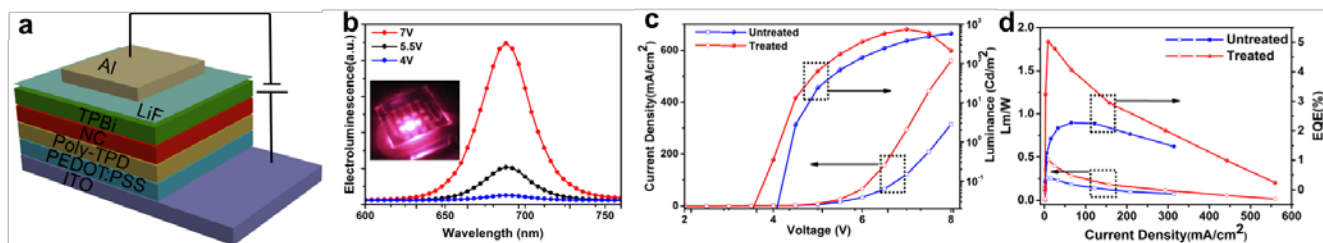


Figure 3. a) Schematic of the device structure of the light emitting diode. b) Electroluminescence (EL) spectra at various applied voltages. The inset shows a photograph of a working PLED. c) Current density-voltage (J-V) and luminance-voltage (L-V). d) Luminous power efficiency - current density and external quantum efficiency - current density (EQE-J) curves of original and IDA-treated CsPbI₃ PLED.

that IDA binds to the NC surface via coordination with the carboxyl group.

To further understand the binding nature of IDA on the NC surface, we performed density functional theory (DFT) calculations assuming a PbI₂-rich (positive charged) CsPbI₃ surface with both OA and IDA passivation (see Figure 2a, b). In both cases, the carboxylic groups can bind to surface Pb atoms with similar charge redistributions after ligand attachment, where the negative charge (blue cloud) is localized on the carboxylic group and the positive charge (red cloud) delocalizes along surface Pb atoms. In the case of the IDA-treated CsPbI₃ surface, the double carboxylic groups can separately bind to two surface-exposed Pb atoms, resulting in a much larger binding energy (1.4 eV) as compared to the single carboxylic-capped surface using an OA ligand (1.14 eV). Moreover, the double carboxylic groups in the IDA ligand could efficiently stabilize the NC surface with fewer surface structural distortions, avoiding the conversion to the undesirable yellow phase at room temperature.

To demonstrate the stability of IDA-treated NCs, we tracked the PL emission over several days (Figure 2c). The PL emission of untreated NCs was almost completely quenched after five days. On the other hand, IDA-treated NCs maintained a constant PL emission with a record value of 90% even after 15 days. Moreover, according to XRD data, no phase change was observed for IDA-treated NCs after 40 days, while untreated NCs essentially transformed into PbI₂ (Figure S9). Significant ligand loss was also confirmed by FTIR for the untreated NCs (Figure S10). A photograph of as-synthesized and 15-days-old NC and IDA-treated NC solutions is presented in Figure 2d. The stability of IDA-treated NCs is also apparent when purifying the samples by anti-solvent wash (see SI). Ethyl acetate (EA) washed untreated NCs exhibit a drop in PLQY down to 60%, while the emission of treated NCs remains relatively unchanged. We ascribe the obvious reduction in PLQY in untreated NCs to the loss of surface ligands from the washing step, due to the more labile nature of the OA surface ligand.²⁴ The amount of OAm on the surface is also reduced after washing (as ascertained from the signal of the two different N 1s core levels of NH₃⁺ to -NH-) reaching a 1:1 ratio with IDA (Figure S11), further confirming the highly stable binding of IDA. We also

note, the IDA ligand passivation process that we devised works well with other halide (Br and Br/I mixtures) perovskite NCs (Figure S12 and Table S2).

Finally, we explored the ability of IDA-treated CsPbI₃ NCs to perform in light emitting devices (PLEDs). We used poly(3,4-ethylenedioxythiophene):poly styrene sulphonate (PEDOT:PSS) on an indium-tin oxide (ITO) glass substrate as the hole-injection layer (HIL) and Poly[bis(4-phenyl)(4-butylphenyl)amine] (Poly-TPD) as a hole-transporting layer (HTL). The electron-transporting layer was 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi). The PLED structure is shown in Figure 3a. The PLEDs show sharp EL peaks under various biases (Figure 3b) with peak wavelengths of 688 nm and a narrow full width at half-maximum of ~33 nm. The peak position is slightly red shifted compared with the PL peak, which we attribute to the inter-dot interaction³⁷ and Stark effect.³⁸ A photograph of the working PLED based on IDA-treated CsPbI₃ shows uniform emission (inset to Figure 3b). Relative to the control NCs, the PLEDs based on IDA-treated CsPbI₃ NCs exhibit higher current density (Figure 3c). This can be explained by the effective electronic coupling between unoccupied molecular orbital (LUMO) of IDA and the conduction band edge of CsPbI₃ NCs (see the calculated project density of states in Figure S13), but not ascribed to the conductive nature of IDA (since IDA has a low conductivity, Figure S14). The turn-on voltages (where luminance is >1 cd·m⁻²) of the original and IDA-treated CsPbI₃ PLEDs are 4.1 V and 4.5 V, respectively. The slightly reduced turn-on voltage indicates better carrier injection into the IDA-treated NCs layer. The maximum luminance of IDA-treated CsPbI₃ PLED reaches 748 cd·m⁻² under the applied voltage of 7 V, which is over two times higher than the control device (314 cd·m⁻² under the same applied voltage). The IDA-treated NC PLED device has a maximum luminous power efficiency of 0.47 lm·W⁻¹, corresponding to a max EQE of 5.02% (8.70 mA·cm⁻²), which is a factor of two better than 0.22 lm·W⁻¹ power efficiency and 2.26% EQE exhibited by the control device (Figure 3d).

In conclusion, we described bidentate ligand passivation of CsPbI₃ NCs that effectively increases their PLQY, leading to near-unity values with a good stability. Our results also suggest that IDA ligands can bind firmly to PbI₂-rich surfaces through dual carboxyl groups,

which can reduce the surface traps and inject extra electrons into NCs. In addition, we achieved similar results with the other halide perovskite NCs, clearly indicating the positive role induced by the bidentate ligand. Moreover, fabricated LED devices based on the IDA-treated CsPbI₃ NCs are broadly superior to devices based on untreated NCs. We believe that our work paves the way for new strategies to increase the stability and charge transport of lead halide perovskite nanostructures with potential applications across optoelectronics devices.

ASSOCIATED CONTENT

Supporting Information.

Materials, synthesis, XPS, NMR, FTIR, HUMO-LUMO calculation and film conductivity measurement.

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