

Polyhedral Oligomeric Silsesquioxane Enhances the Brightness of Perovskite Nanocrystal-Based Green Light-Emitting Devices

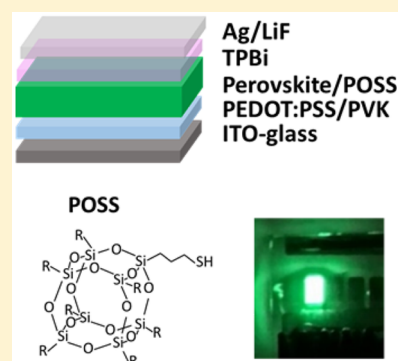
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Supporting Information

ABSTRACT: The beneficial role of the insulating material polyhedral oligomeric silsesquioxane (POSS) as a solution additive or an additional hole-blocking layer to enhance the performance of electroluminescent green light-emitting devices (LEDs) based on CsPbBr₃ perovskite nanocrystals is demonstrated. POSS improves the surface coverage and the morphological features of the films deposited either from supernatant or suspension of perovskite nanocrystals. The external quantum efficiency and the luminance efficiency of LEDs with an additional POSS layer reach 0.35% and 1.20 cd/A, respectively, constituting a more than 17-fold enhancement to the reference devices without POSS; the LED peak luminance reaches 2983 cd/m², and the device stability is improved. The POSS acts as a hole-blocking layer between the perovskite nanocrystals and TPBi, keeping both electrons and holes located within the active layer for an efficient recombination.



Room-temperature perovskite-based light-emitting devices (LEDs) were reported by Friend's group in 2014,¹ after the first demonstration of a low-temperature device in the 1990s.² After these early works, perovskite-based LEDs have attracted a great deal of attention with many more groups joining this field, leading to a burgeoning number of research papers.^{1,3–30} Among these, research on inorganic cesium lead halide perovskite nanocrystals (NCs) of a general composition CsPbX₃ (X = Cl, Br, and I or mixed halide) has become dominant because of their high photoluminescence (PL) quantum yield, which reaches 90% in solution; easy solution processing; and narrow emission peaks with a full width at half-maximum (fwhm) that is typically 20 nm or less.³¹ Perovskites are unique in that their intrinsic defects do not appear to act as electronic trap states,³² and tuning the size or halide compositions of perovskite NCs enables the adjustment of emission colors across the entire visible range.^{33–38} These outstanding material properties offer great potential for CsPbX₃ NCs as emissive materials in electroluminescent (EL) devices.^{3,4,8,10–13,25} However, the as-prepared CsPbBr₃ NCs have some limitations for direct use in LEDs fabrication, thus far usually displaying low brightness and efficiency. The film quality is relatively poor because of the solubility of the perovskite NCs in toluene, while the poor conductivity of their commonly used long-chain surface ligands (such as oleic acid and oleylamine) hamper the efficiency of charge injection. The low solubility of perovskite NCs leads to partial, patchy film coverage over the device sublayers. Simply increasing the NC loading in the coating solution means that the associated increase in the poorly conducting ligand content significantly

increases device resistance. We found that trying to remove ligands by a number of reprecipitation cycles tends to exacerbate the solubility problem. This has led us to take a novel approach to combat these two inter-related problems by introducing an additive polyhedral oligomeric silsesquioxane (POSS) that improves the solubility of perovskite NCs and simultaneously contributes to balanced carrier conductivities in the resulting LEDs.

POSS has a cage-like molecular structure with an inorganic siloxane core and eight surrounding organic corner groups.³⁹ It has high chemical stability and optical transparency in the ultraviolet (UV) as well as visible spectral ranges and has been widely used in biomedical applications,⁴⁰ to formulate cross-linked resins,⁴¹ as a building block for zeolite-like materials,⁴² and so forth.⁴³ Our group previously demonstrated the use of POSS as a surface ligand for CdSe NCs⁴⁴ and as a protective coating for carbon dots.⁴⁵ In our recent paper, we also showed that POSS can overcome the poor water resistivity of perovskite NCs by blocking the undesirable anion exchange reactions as a protective ligand matrix, making it possible to fabricate all-perovskite down-conversion white LEDs by using green-emitting and red-emitting NC powders as solid-state luminophores.¹² Here, we demonstrate the significant improvement of film-forming properties and the enhancement of the performance of CsPbBr₃ NC-based LEDs by using POSS as a

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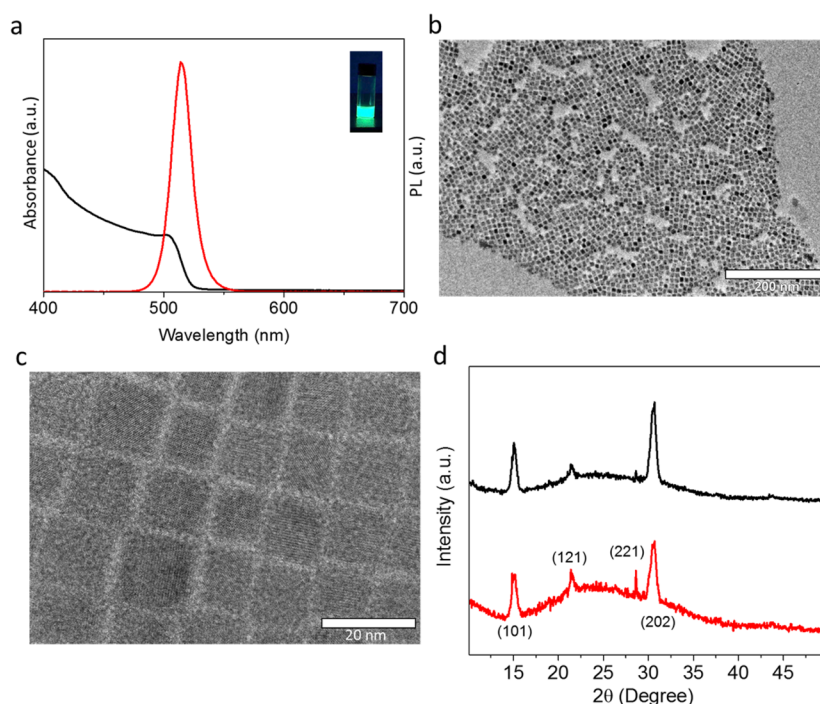


Figure 1. (a) UV–vis absorption and PL (370 nm excitation wavelength) spectra of CsPbBr₃ NCs dissolved in toluene, with inset showing a photograph of a NC solution under 365 nm UV irradiation. (b) TEM image of CsPbBr₃ NCs with large areas of nearly monodisperse cubic particles. (c) HRTEM image of perovskite CsPbBr₃ NCs mixed with POSS. (d) XRD spectra taken from spin-coated films of perovskite NC suspension (black line) and the same perovskite NCs treated with 0.5 mg/mL POSS (red line).

solution additive. We also used POSS as an additional thin layer to balance electron–hole injection of LEDs, as well as an additive in the perovskite NC emissive layer, all resulting in the improvements of brightness, external quantum efficiency (EQE), and the luminance efficiency (LE).

CsPbBr₃ NCs were synthesized by Kovalenko’s method³⁵ as described in the Supporting Information. Because of the well-documented tendency of as-synthesized perovskite NC solution to partially precipitate in the form of larger agglomerates,³⁷ we distinguish between the two types of samples in the following studies: a supernatant obtained by standing the as-prepared NC solution for 10 min prior to use so that its upper part (supernatant) is crystal clear and free from any precipitate causing visible light scattering and a suspension obtained by shaking the partially precipitated solution for 1 min to form a turbid liquid. We estimated the concentration of perovskite NCs by weight in the supernatant and suspension solutions as 1 and 50 mg/mL, respectively. Figure 1a shows the UV–visible absorption and PL spectra of CsPbBr₃ NCs in supernatant; they exhibit no light scattering and a bright green emission (as seen excited by a 365 nm UV lamp in the inset photo) with high color purity (fwhm of the PL peak equal to 20 nm). The transmission electron microscopy (TEM) image of CsPbBr₃ NCs from the supernatant (Figure 1b) shows nearly monodisperse cube-shaped particles with an edge length of 9–10 nm. For the POSS-treated samples, different amounts of mercaptopropylisobutyl POSS (see Table 1) were added into the perovskite NC solutions, which were stirred for 1 min allowing the attachment of POSS onto the surface of the NCs¹² before deposition of films. The addition of POSS to perovskite NC solutions did not affect their absorption and PL spectra¹² or alter the shape of perovskite NCs as seen in the HRTEM image of Figure 1c. XRD patterns were measured on films spin-coated onto glass substrates from the perovskite NC suspension

Table 1. Different Solution Types and Compositions Used to Form Perovskite NC-Based LEDs, and the Corresponding Device Performances, Including Maximum Luminance, External Quantum Efficiency (EQE), and Luminance Efficiency (LE)

solution type	max. luminance (cd/m ²)	max. EQE (%)	max. LE (cd/A)
supernatant			
NC	430	0.10	0.34
NC + 0.01 mg/mL POSS	597	0.34	1.15
NC + 0.05 mg/mL POSS	720	0.26	0.87
NC + 0.1 mg/mL POSS	1137	0.32	1.08
NC + 0.5 mg/mL POSS	476	0.33	1.12
suspension			
NC	376	0.02	0.07
NC + 0.01 mg/mL POSS	1882	0.08	0.26
NC + 0.05 mg/mL POSS	1869	0.08	0.29
NC + 0.1 mg/mL POSS	2585	0.10	0.35
NC + 0.5 mg/mL POSS	1989	0.12	0.39
POSS as an additional hole-blocking layer			
NC/POSS/TPBi	2983	0.35	1.20

solutions both with and without added POSS. Figure 1d shows almost no changes in the line positions and widths in the XRD patterns. The marked peak positions in Figure 1d are consistent with the reference positions of previously published data for CsPbBr₃ NCs.³⁵

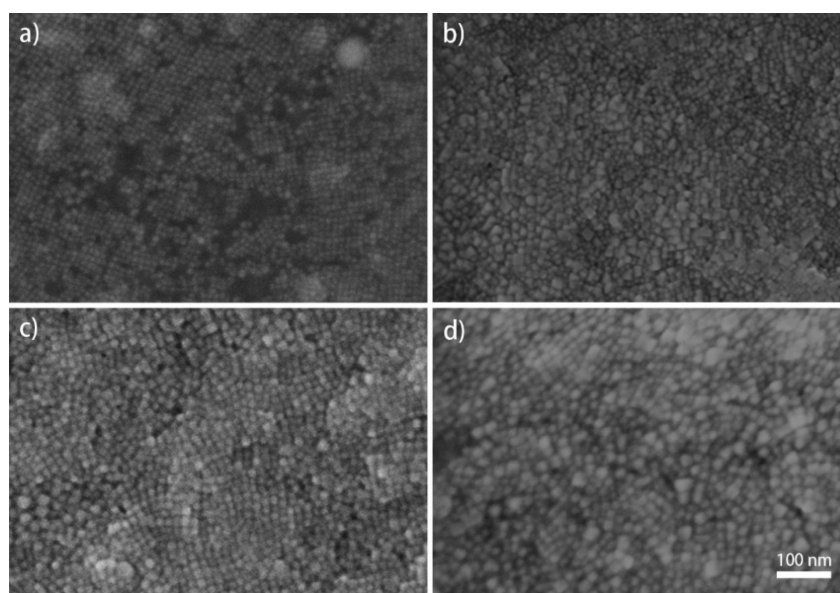


Figure 2. Top view SEM images of spin-coated CsPbBr₃ perovskite films based on (a) NC supernatant, (b) NC suspension, (c) NC supernatant with addition of 0.5 mg/mL POSS, and (d) NC suspension solution with an additional POSS layer deposited on top.

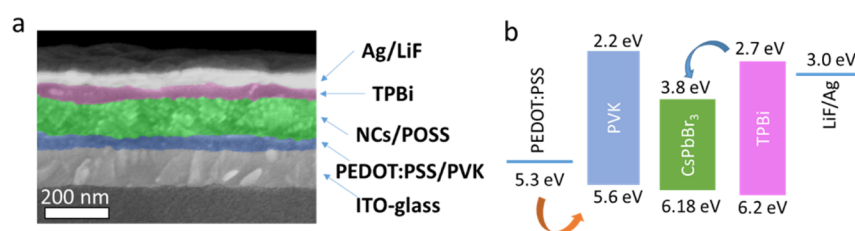


Figure 3. (a) Cross-sectional SEM image and a device structure of the CsPbBr₃ NC-based LED, with (b) the corresponding energy band diagram. The color coding is similar in panels a and b.

To fabricate perovskite-based LEDs, several different solution types (as specified in the caption of Figure 2) have been spin-coated onto PEDOT:PSS/PVK coated ITO-glass and imaged with top view scanning electron microscopy (SEM) to analyze the quality of the films. As seen in Figure 2a, perovskite NC films spin-coated from the supernatant solution (NC concentration around 1 mg/mL) could not fully cover the underlying substrate, leaving many uncovered regions. To acquire denser films, the suspension solution (NC concentration around 50 mg/mL) was used, which indeed resulted in complete substrate coverage (Figure 2b). Figure 2b also shows that it is hard to observe cubic-shaped NC in the deposited films, due to the prevalence of larger, irregularly shaped perovskite particles formed because of the agglomeration of NCs in the supernatant. As previously reported, POSS derivatives containing thiol groups can efficiently attach to perovskite NCs¹² and contribute to formation of more uniform films. Indeed, by adding POSS to the spin-coating solution, we were able to use the supernatant solution to obtain dense films with good coverage. As seen in the SEM image in Figure 2c, all the substrate was fully covered with NCs while most of them remained visibly cubic in shape. Finally, we also prepared films where a POSS layer has been deposited by spin-coating on top of the perovskite NCs spin-coated from the suspension solution before thermally evaporating the TPBi layer for an LED structure (Figure 2d). Compared with Figure 2b (the layer deposited from NC suspension without addition of POSS), Figure 2d still allows us to distinguish irregular nanoparticle

agglomerates, albeit with less contrast because of the thin POSS coverage on top. We have used cross-sectional SEM images (Figure S1) to determine the thicknesses of perovskite NC films with and without POSS spin-coated on ITO-glass from the NC suspension solutions, which were in the range of 110–120 nm in both cases.

On the basis of the film quality findings, we fabricated similar full LED structures of ITO-glass/PEDOT:PSS/PVK/CsPbBr₃ perovskite NCs/TPBi/LiF/Ag, with a cross-sectional SEM image of a representative sample shown in Figure 3a. A patterned indium tin oxide (ITO) layer served as the anode, PEDOT:PSS film as the hole injection layer, poly(*N*-vinyl-carbazole) (PVK) film as the hole transporting layer, CsPbBr₃ NC film as the emissive layer, 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene (TPBi) film as the electron-transporting layer, and LiF/Ag as the cathode. Figure 3b shows the energy-level diagram for the LED constituting materials, with the energy level values taken from ref 46 (PVK), ref 3 (CsPbBr₃), and ref 47 (TPBi).

The different solution types and compositions used to form perovskite NC LEDs and the corresponding device performance are summarized in Table 1. The luminance of LEDs fabricated from the spin-coated supernatant solutions of NCs is around 430 cd/m² (Figure S2a,b) with a peak EQE around 0.1%. The reason for the relatively low brightness and efficiency of these devices may be primarily related to a sparse, thinly covered active layer of perovskite NCs (Figure 2a). However, for the denser and thicker films obtained from suspension NC

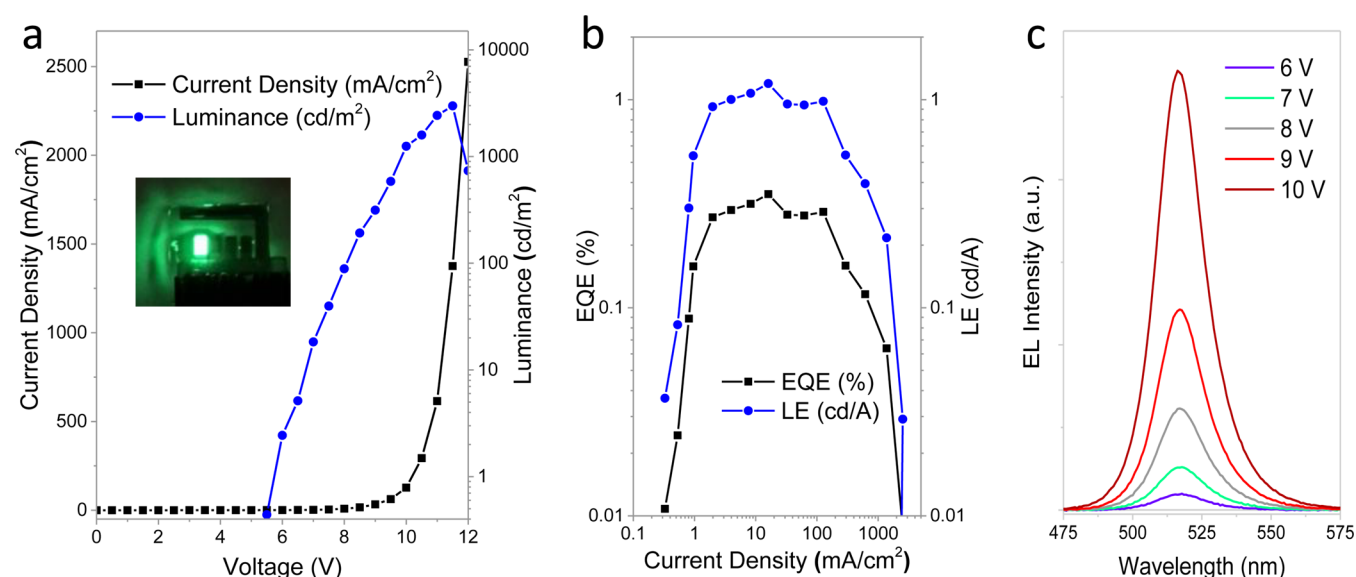


Figure 4. (a) Current density and luminance vs driving voltage (inset shows a photograph of a working device operated at 8 V); (b) EQE and LE vs current density; (c) EL spectra under different applied voltages for LEDs fabricated from NC suspension solution with an additional POSS layer between the perovskite NC and TPBi layers.

solution, even though a fully covered surface coverage was obtained (Figure 2b), the LED performance was still on a par with, and even lower than, the supernatant solution device, typically 376 cd/m² luminance (Figure S2 c,d). However, the major difference between the supernatant and suspension devices lies in their EQEs (0.1% and 0.02%, respectively). The latter exhibits lower EQE due to overall higher film resistance resulting from the formation of the large domains observed by SEM in Figure 2b with the greater proportion of poorly conductive perovskite NC ligands (as confirmed by thermogravimetric analysis).

As discussed above in relation to Figure 2c, the addition of POSS to the supernatant NC solution greatly improves the substrate coverage, which may be helpful for improved LED brightness. Because POSS is an insulator, only a low concentration of 0.1 mg/mL in supernatant solution was used, based on the optimization studies on CsPbBr₃ LEDs, as shown in Figure S3a–d. The luminance of the resulting device has been improved to 1137 cd/m², and the EQE (0.32%) was also three times that of the supernatant solution without POSS (0.1%). In suspension NC solution where large domains were formed, POSS addition was effective in breaking inter-NC attachments to separate NCs. A small amount of POSS dissolved in the spin-coating supernatant solution helped to maintain the shape of the NCs and prohibit the formation of larger aggregates, as observed in Figure 2b. Taking advantage of the higher NC loading and the preserved separate NCs, the overall brightness of these LEDs reached higher values for optimized POSS concentrations (Figure S3e–h). The best luminance (2585 cd/m²) was obtained for a POSS weight concentration of 0.1 mg/mL. This brightness is comparable to the best-performing perovskite NC devices recently reported in the literature⁴ and constitutes an almost 2-fold improvement upon the value in our own recent paper.³ The EQE of this device, however, is still low (0.1%) because of the poor conductivity of the ligands and the additional POSS in the films.

To provide information on recombination pathways in the active perovskite NC layers, PL decay curves of the CsPbBr₃

NC films deposited from different types of NC solutions (with and without addition of POSS) on glass/PEDOT:PSS coated ITO substrates were recorded and analyzed (Figure S4). The average PL decay lifetimes for original supernatant and suspension NC solutions were found to be 115 and 434 ns, respectively. Under the assumption that both types of solution have similar PL quantum yields, this would indicate a higher electron–hole recombination rate for the supernatant NCs, which suggests that the higher EQE of the respective LEDs may arise from the higher radiative recombination rate for the supernatant case. When additional POSS was introduced into the supernatant and suspension NC solutions, the average PL lifetimes became shorter (from 434 to 134 ns for the suspension solution, and from 115 to 63 ns for the supernatant solution). Adding the POSS as a separate layer with the NC suspension as the active layer does not reduce the average PL decay times as strongly as adding POSS within the active layer (the lifetime decreased from 434 to 342 ns), though it does bring a 21% increase in average recombination rate. However, it must be kept in mind that if the interaction of POSS with the NCs is singularly responsible for this improvement then the interface between the two layers is where this benefit will be localized. However, the PL measurements will measure an average of the lifetimes in this contact layer and those from the rest of the NC film, the latter being closer to the 434 ns for the structure without POSS. The likely improvement in the recombination rate due to the contact with POSS (again assuming no great difference in the nonradiative recombination rates) is therefore probably much greater than the 21% improvement would appear to show.

In the light of these findings, we have found that adding POSS to the spin-coating solutions improves the morphology and coverage of the perovskite NC layers, and while this can improve the PL and the EQE of LEDs in some cases, this is not accompanied by a large improvement in the luminance of LEDs because of the limitations in the film conductivity when introducing an essentially insulating additive. However, the use of POSS as a separate additional layer brings far greater benefits to the EQE and the maximum luminance together. The

additional benefit is believed to arise from the effect of the POSS layer as a hole-blocking layer between the perovskite NCs and TPBi layers. This will help to keep both electrons and holes located within the NC layer for recombination: the highest occupied molecular orbital (HOMO) level of POSS is more negative than TPBi while the lowest unoccupied (LUMO) level for PVK helps to block electron flow out of the NC layer at the opposite side of the active region. The carrier recombination zone is therefore better localized within the active layer. Without the separate POSS layer, the offset between the valence level of the NCs and the HOMO level of TPBi layer is only -0.02 eV, and this may be an ineffective hole barrier at room temperature. In this respect the POSS layer is performing the same function as the thin film of perfluorinated ionomer sandwiched between the hole-transporting layer and perovskite emissive layer as reported in our previous work.³ A similar mechanism has been suggested for the quantum dot-based LEDs while employing a thin insulating layer of poly(methyl methacrylate).⁴⁸ The SEM of the ITO/NCs/POSS cross section in Figure 2d shows the clearly recognizable NC layer morphology, the fully covered surface, and relatively uniform appearance.

We thus fabricated perovskite-based LEDs with an additional POSS film employed as a hole-blocking layer deposited between the perovskite NCs (from the nontreated suspension solution) and TPBi layers, whose performance characteristics are presented in Figure 4 and summarized in Table 1. The current density and luminance versus driving voltage of the device (Figure 4a) indicate a turn-on voltage (luminescence above 1 cd/m^2) of around 5.8 V , which is lower than for all the devices without the POSS layer (about 6.5 V). Moreover, the peak luminance of 2983 cd/m^2 obtained at 11.5 V was almost 8 times greater than that of the LED fabricated using a spin-coated suspension solution of perovskite NCs (Table 1). Reproducibility tests have been performed, with over 80% of the 30 LED devices in the same batch providing brightness over 2900 cd/m^2 . As shown in Figure 4b, the EQE and the LE of the champion device with the additional layer of POSS were 0.35% and 1.20 cd/A , respectively, which very favorably compares with the figures for the respective perovskite NC-based LEDs made from the suspension solution without POSS (0.02% and 0.07 cd/A ; more than 17-fold enhancement for both parameters). Figure 4c shows the EL spectra of a perovskite NC-based LED with an additional POSS layer at different applied voltages. The peak position of the EL spectra remains stable at 517 nm between V_{on} (5.8 V) and the operating voltage for the maximum brightness (11.5 V). The fwhm of the EL spectrum is just 18 nm , which is the same as in our previous report,³ and the Commission Internationale de l'Eclairage (CIE) color coordinates of the LED device are (0.11, 0.77), which exceeds the National Television Standards Committee (NTSC) standard green value for display applications.⁴⁹

The EL stability of several kinds of perovskite NC-based LEDs was evaluated by measurements conducted in air with 50% relative humidity in a dark room, under constant voltage of 7.0 V applied on devices while monitoring the EL intensity. During the stability measurements on POSS-containing samples, no change in the shape of the EL spectra was observed, while devices without POSS experienced a fast dropping of the EL signal, which diminished completely after 2 min (Figure S5). Such fast EL quenching (50% of EL signal drop within a few tens of seconds) was previously observed in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ based perovskite LEDs measured under the

same conditions.⁵⁰ Devices with a POSS hole-blocking layer had a 5 times longer operation lifetime.

In conclusion, we demonstrated the beneficial role of an insulating material POSS as a solution additive to enhance the performance of electroluminescent CsPbBr_3 NC-based LEDs. The POSS improves the surface coverage and the morphological features of the films deposited either from supernatant or suspension of perovskite NCs. Deposition of POSS as a hole-blocking layer results in the LED peak luminance of 2983 cd/m^2 at 11.5 V , being almost 8 times greater than that of LEDs fabricated by simply spin-coating supernatant solutions of NC without a hole-blocking layer. The EQE and the luminance efficiency of LEDs with an additional POSS layer reach 0.35% and 1.20 cd/A , respectively, constituting a more than 17-fold enhancement to the reference devices without POSS, and the device stability was also improved. The use of POSS as a separate additional layer brings far greater benefits to the EQE and maximum luminance together, indicating the effect of POSS as a hole-blocking layer between the NCs and TPBi in keeping both electrons and holes located within the active NC layer for more efficient recombination.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b02224.

Experimental details, cross-sectional SEM images of films, performance characteristics of different LED devices, and EL stability measurements for different LED types (PDF)

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Notes

The authors declare no competing financial interest.

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