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Crown Ethers Enable Room Temperature Synthesized CsPbBr₃ Quantum Dots for Light- Emitting Diodes

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ABSTRACT The synthesis of all-inorganic cesium lead halide perovskite quantum dots (QDs) typically requires high temperatures, stringent conditions, large quantities of surface ligands, and judicious purification steps to overcome ligand-induced charge injection barriers in optoelectronic devices. Low-temperature syntheses generally require lower ligand concentrations, but are severely limited by the low solubility of the Cs precursor. We describe an innovative and general approach under ambient conditions to overcome these solubility limitations, by employing crown ethers. The crown ethers facilitate complete dissolution of the CsBr precursor, rendering CsPbBr₃ QD inks practical for device fabrication. The resultant LEDs displayed bright green emission, with a current efficiency, and external quantum efficiency of 9.22 cd A⁻¹ and 2.64%, respectively. This represents the first LED based on CsPbBr₃ QDs prepared at room temperature. Lastly, the crown ethers form core-shell structures, opening new avenues to exploit their strong coordination strength.

In recent years, lead halide perovskites have emerged as extraordinary optoelectronic materials in photovoltaic and light-emitting applications.¹⁻⁵ In particular, fully inorganic cesium lead bromide (CsPbBr₃) nanocrystals show great potential for incorporation in light-emitting diodes (LEDs) by virtue of near-unity photoluminescence quantum yields (PLQY), narrow emission widths, high structural stability, and compositional versatility. Typically, these quantum dots (QDs) are prepared via the hot-injection synthesis at temperatures in excess of 150 °C.⁶⁻⁸ The long-chain ligands, employed to solubilize the precursors while subsequently stabilizing the final QDs, affect the size and morphology of the as-prepared materials greatly.^{7, 9} Moreover, the high concentration of ligands required during synthesis, may further impede the charge injection during operation in LEDs, severely limiting the devices efficiencies, despite their high PLQY. To overcome this injection barrier, judicious purification and/or surface engineering steps are required, boosting the external quantum efficiency (EQE) 50-fold.^{8, 10-13} Apart from the abundant reports on high temperature methods, limited protocols to form CsPbBr₃ QDs at room temperature are reported,¹⁴⁻¹⁸ although most are reliant on the use of pre-synthesized Cs-oleate (i.e. prepared under similar conditions to the hot injection method).¹⁶⁻¹⁸

Low-temperature techniques are generally based on the ligand-assisted reprecipitation protocol (LARP),¹⁹ whereby the dissolved molecular precursors are injected into a noncoordinating solvent in the presence of coordinating ligands. Generally, this method requires a lower ligand concentration to form a stable colloidal QD solution than the hot-injection method, however, it is severely limited by the low solubility of the Cs precursor in polar media (such as *N,N*-dimethylformamide, DMF, or dimethylsulfoxide, DMSO). The resultant low reaction yields are generally impracticable for LED device fabrication, and to the best of our knowledge no LEDs

based on low-temperature prepared CsPbBr₃ QDs have been reported to date. A protocol which overcomes the aforementioned limitations is thus highly desired.

Herein, we describe an innovative and general strategy employing crown ethers (CE), in particular dibenzo-21-crown-[7] (DB21C7; **Figure 1a**), to facilitate the dissolution of CsBr in DMF up to concentrations of 0.1 mol dm⁻³; ca. 4 times higher than the reported solubility in DMF without the addition of crown ethers.²⁰ This overcomes previous solubility limitations, and renders precursor solutions with concentrations practical for device fabrication.

Figure 1. (a) Structural formula of dibenzo-21-crown-[7] and (b) complexation of Cs cation via weak van der Waals interactions with the lone electron pairs in DB21C7. (c) ¹H NMR spectra of DMF (black), DB21C7 dissolved in DMF (red), and CsBr dissolved in a mixture of DB21C7/DMF (blue), respectively. *N,N*-dimethylformamide-D₇, containing 0.05% v/v tetramethylsilane, was used as internal standard. A weak chemical shift of $\Delta\delta$ +0.01-0.05 ppm (i.e. de-shielding) is observed for all peaks upon complexation with the Cs cations. The peak numbers correspond to the protons in (a). For clarity, an offset is used between the spectra.

Crown ethers are cyclic molecules comprising of a ring (or multiple rings) of ether groups that show a remarkable selectivity to bind certain alkali metal ions via hydrogen bonding,^{21, 22} whereby the selectivity is mostly determined by the size of the ring structure. We have rationally chosen the DB21C7 as its cavity is of sufficient size (3.4-4.3 Å) to coordinate the Cs⁺ cations (3.3 Å)²³ via weak van der Waals interactions with the lone electron pairs of the oxygen atoms within the ring structure (Figure 1b), forming a host-guest complex, thus facilitating its solubilization in DMF. The complexation was subsequently verified by proton nuclear magnetic resonance (¹H NMR), where weak chemical shifts of approximately $\Delta\delta$ +0.01-0.05 ppm were observed upon coordination (Figure 1c).

Following the complexation, spherical CsPbBr₃ QDs were fabricated through a modified LARP protocol at room temperature, in which the dissolved Cs precursor (Cs:DB21C7 = 1:1) was added to a vigorously stirring solution containing toluene, *n*-octylamine (OctAm), and oleic acid (OA). The obtained QD solution was purified through centrifugation for 10 min at 10000 rpm, after which the supernatant phase was discarded and the precipitate redispersed in 300 μ L toluene. Following a second centrifugation step, for 10 min at 1000 rpm, the resultant supernatant phase (stable for >2 weeks under ambient conditions) was used for further characterization and device fabrication. It should be noted that the CsPbBr₃ QDs did not form in absence of the crown ether or when off-stoichiometric ratios Cs:DB21C7 were employed during the synthesis. The obtained QDs were highly crystalline and of spherical morphology (**Figure 2a and Figure S1**). The orthorhombic crystal structure of the QDs (*Pnma* space group)²⁴ was confirmed by X-ray diffraction (XRD; see **Figure S2**) and selected-area electron diffraction (SAED; inset Figure 2a). Further analysis on the crystallite sizes showed a bimodal size distribution for the as-synthesized QDs (Figure 2b), with the two populations centered at

approximately 4.5 and 6.4 nm, respectively. In view of the Bohr diameter of CsPbBr₃ (ca. 7 nm),⁶ quantum confinement is expected. The steady-state photoluminescence (PL) and absorbance spectra (Figure 2c; black lines) clearly show two distinct emission/absorption features. A double Gaussian peak fit (see **Figure S3**) of the PL emission showed two peaks centered at 490 nm (FWHM ~14.8 nm) and 515 nm (FWHM ~23.6 nm), related to the two different particle size distributions centered at 4.5 and 6.4 nm, respectively. Despite the small QD sizes, the quantum-size effect is not as strong as expected. For example, Protesescu et al. demonstrated a band gap of ca. 2.7 eV (~460 nm PL emission) for 3.8 nm-sized crystals.⁶ This suggests that the smallest QDs do not significantly contribute to the PL emission, while the signal at 515 nm originates from the larger crystals within the size distribution (viz. ~6 nm). At increased excitation wavelengths a narrowing of the PL emission peak at 515 nm is observed (**Figure S4**), further corroborating that the emission predominantly arises from the larger QDs. The average fluorescence lifetimes were determined for both the 490 and 515 nm emission peaks using time-resolved spectroscopy. The former displayed an ultrafast average lifetime of 1.00 ns, whereas the signal at 515 nm showed an increased lifetime of ca. 4.76 ns, respectively. The ultrafast decay of the smallest QDs probed at 490 nm, can be attributed to the high concentration of surface defects trap states (i.e. high surface-to-volume ratio), which further confirms their limited contribution to the overall PL signal. Interestingly, the addition of a small quantity of *n*-butanol (BuOH) during the synthesis resulted in a single (albeit broader) size distribution with an average crystallite size of ca. 6.6 ± 2.1 nm, and a significantly enhanced average lifetime of approximately 11.5 ns (single PL emission peak at 515 nm; see **Figure S5**). Notwithstanding the increased PL intensity, the significant drop in QD concentration caused by the BuOH rendered the ink unfavorable for device fabrication.

Figure 2. Structural characterization of purified CsPbBr₃ QDs prepared via complexation with dibenzo-21-crown-[7]. **(a)** HRTEM image of ensemble CsPbBr₃ QDs (additional images in Figure S1). Inset: selected-area electron diffraction (SAED) pattern obtained from a large ensemble of QDs (scale bar corresponds to 2 nm⁻¹). The obtained lattice spacings corroborate with the XRD pattern in Figure S2. Photo: cuvette containing dilute QDs solution in toluene under ambient light (top) and UV illumination (bottom). **(b)** Crystallite size distribution obtained from low-magnification HRTEM images, displaying a double distribution centered at ca. 4.5 nm and 6.4 nm. **(c)** Normalized PL (solid line) and absorbance (dashed line) spectra at $\lambda_{\text{EX}} = 350 \text{ nm}$, respectively. **(d)** Time-resolved PL decays (using $\lambda_{\text{EX}} = 405 \text{ nm}$) collected at $\lambda_{\text{EM}} = 490 \text{ nm}$ (black) and $\lambda_{\text{EM}} = 515 \text{ nm}$ (blue), respectively.

A closer inspection of the as-formed QDs with HRTEM revealed, surprisingly, the existence of a ~ 7.8 Å thin shell surrounding the crystallites (**Figure 3a**), which represents the first direct observation of halide perovskite core-shell QDs. Previously, nonlinear optical spectroscopy was employed to indirectly confirm the existence of a (OA)₂PbBr₄ shell material on CH₃NH₃PbBr₃ QDs,^{25, 26} as direct observation in HRTEM was improbable due to the lack of electron density difference between the aforementioned phases. Similarly, the amine and fatty acid ligands used here, have not shown shell formation during the CsPbBr₃ synthesis.^{6, 7, 16} We therefore postulate that our shell material consists of DB21C7 molecules through π - π stacking of the outer phenyl groups (see Figure 1a), rather than aliphatic amine and carboxylate ligands. Fourier-transform infrared (FTIR) confirmed that DB21C7 still forms a complex after QD purification, as observed from the shift in the ν (C-H) stretching vibrations from 2931 and 2878 cm⁻¹ to 2924 and 2853 cm⁻¹, respectively (Figure 3b). Interestingly, the presence of the ν (C=O) peak at 1709 cm⁻¹ and the concurrent absence of asymmetric stretching ν (COO⁻) between 1500 and 1620 cm⁻¹, implies that the oleic acid is not deprotonated. This can be explained by the low thermal energy of the system at room temperature, which favors hydrogen bonding between the oleic acid and the CE over deprotonation (i.e. the formation of a carboxylate anion). Notably, the observed shell thickness corresponds well with the size of the crown ether (see Figure 3c). The clear phase contrast between the core and shell thus likely originates from the great number of oxygen atoms in the DB21C7 close to the core's surface. Based on our observations, we believe that the QD formation proceeds in several successive steps (see Figure 3c). Firstly, the Cs⁺ cations are strongly coordinated by the DB21C7 molecules in the precursor solution. Following the injection into the noncoordinating solvent, the CsPbBr₃ instantly precipitates. Here, we anticipate that the CE-CsPbBr₃ complex forms a stable 'seed particle', whereby the electronegativity matching

between the CsPbBr₃ and DB21C7 imparts a repulsive force between the ligands and as-formed seeds. This effectively places the ligands on the outer part of the CE, forming a structure similar to micelles. Next, the coordinative π - π stacking of the outer phenyl groups of DB21C7 places seeds in each other's proximity, allowing for some coalescence, growth, and ligand reorganization, finally resulting in the formation of core-shell CsPbBr₃-DB21C7 QDs capped by ligands. To further strengthen our hypothesis, we added a small amount of BuOH during the QD synthesis. Here, we expect the presence of the alcohol to disrupt the dynamic ligand binding due to the strong interaction between the polar BuOH solvent and DB21C7. Indeed, after the addition of BuOH, we also observe QDs without a shell (inset Figure S5a). The temporary instability caused by the partial dissolution of DB21C7 allows for QDs growth through coalescence (Figure S5b), and redistribution of the OctAm and OA ligands on the QDs' surface. This is further corroborated by the observed PL intensity increase²⁷ and lifetime enhancement after BuOH usage (see Figure S5d). More study is required, however, to fully understand the reaction mechanism and subsequent shell formation and ligand reorganization.

Figure 3. (a) HRTEM image (close-up) of small ensemble of CsPbBr₃ QDs. The QDs display a high degree of crystallinity, with clearly visible shells formed on the outside of the crystal, as marked by white arrows. (b) Fourier-transform IR spectra of dibenzo-21-crown-[7] powder (black) and spincoated thin film of purified CsPbBr₃ QDs on glass (blue). (c) Schematic representation of the QD and shell formation.

Finally, two sets of green-emitting LEDs were fabricated from the purified QD inks, based on single and double layer deposition of the inks (refer to Supporting Information for more details). The LEDs show excellent diode behavior, with low leakage current ($< 1 \mu\text{A cm}^{-2}$) and sharp turn-on around 2.5 V, as shown in the current density-voltage-luminance (J-V-L) plot (**Figure 4a**). The device configuration comprises indium-tin oxide (ITO)/PEDOT:PSS/CsPbBr₃ QDs/PO-T2T/Ca/Al (refer to Supporting Information for detailed device fabrication protocol), with

PEDOT:PSS, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), and PO-T2T, (2,4,6-Tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine), acting as hole- and electron transporting layer, respectively. The small bump observed in the J-V curve at ca. 1.8 V may originate from the DB21C7 shell, impeding efficient current flow. This effect is slightly larger for the double layer device, which further developed in decreased slopes at higher voltages in both J-V and L-V curves.

Figure 4. LED Device characteristics using single and double emitter layers. **(a)** Current-voltage-luminance (J-V-L) characteristics of CsPbBr₃ QD LEDs. Inset: photograph of working LED device at 4 V. **(b)** Electroluminescence spectrum at various driving voltages. The EL peak is positioned around 519 nm with a FWHM of ca. 22.6 nm, corresponding to CIE 1931 color coordinate (0.20, 0.76). Inset: EL spectra in logarithmic scale. **(c-d)** Characteristic current efficiency/EQE versus luminance plots, respectively (active device area: 3 mm²).

Table 1. Summary of the maximum luminance, current efficiency, and EQE of the single/double layer LED devices compared to reported values.

Synthesis	EL	Turn-on	Luminance	Current	EQE	Reference	Notes
Temp.		Voltage		Efficiency			
(°C)	(nm)	(V)	(cd m ⁻²)	(cd A ⁻¹)	(%)		
RT	519	2.5	14454	4.29	1.27	This Work	DB21C7 ^{b)} ; single layer
RT	519	2.5	3880	9.22	2.64	This Work	DB21C7 ^{b)} ; double layer
130	527	4.6	3853	8.98	2.21	[¹³]	CsPbBr ₃ -CsPb ₂ Br ₅ QDs
150	515	~4.0	7493	3.71	0.81	[²⁸]	CsPbBr ₃ (without Mn-doping)
150	512	~4.4	9971	6.40	1.49	[²⁸]	Stabilization with ~4% Mn-doping
170	516	4.2	946	0.43	0.12	[²⁹]	First reported CsPbBr ₃ QD LED
170	523	2.6	2335	n.r. ^{a)}	0.19	[¹¹]	Cross-linking with TMA ^{c)}
170	512	3.4	15185	13.3	6.27	[⁸]	Hexane/ethylacetate treatment
180	515	3.0	330	~9	3.00	[¹²]	Surface engineering with DDAB ^{d)}
190	517	5.8	2983	1.20	0.35	[¹⁰]	POSS matrix ^{e)}

^{a)}n.r. = not reported; ^{b)}DB21C7 = dibenzo-21-crown-[7]; ^{c)}TMA = trimethylaluminium; ^{d)}DDAB = di-dodecyl dimethyl ammonium bromide; and ^{e)}POSS = polyhedral oligomeric silsesquioxane.

The lower maximum luminance of the thicker film (3880 cd m⁻²) compared to the thinner film (14454 cd m⁻²) is most likely related to reabsorption phenomena, whereas the lower current density implies lower leakage currents due to improved surface coverage. The electroluminescence (EL) spectra (Figure 4b) show a peak maximum at 519 nm, which constitutes a 4 nm red-shift compared to the PL of the colloidal solution. Interestingly, the contribution at 490 nm is still observed, suggesting that an energy cascade from the smallest QDs (i.e. high bandgap) to the larger QDs (i.e. low bandgap) is impeded.³⁰ Lastly, the devices based on the double deposition displayed fair temporal stability of ca. 555 s (i.e. luminance half-life)

when operated at ca. 120 cd m⁻² (see **Figure S6**), with an increased current efficiencies (CE) and external quantum efficiencies (EQE) of 9.22 cd A⁻¹ and 2.64%, respectively, placing them among the best QD LED devices currently reported (see Figure 4c,d and **Table 1** for device summary and comparison with reported CsPbBr₃ QD LEDs).^{8, 31-33}

To conclude, we have demonstrated a generic strategy to overcome the low solubility of Cs precursors in polar media by employing crown ethers. This allowed for the synthesis of CsPbBr₃ QDs under low temperature conditions and their first utilization in efficient and bright LEDs. The use of crown ethers during synthesis resulted in the formation of core-shell QDs, with the former as shell material. The strong coordinative strength and selectivity of the crown ethers may open a new avenue to synthesize different types of halide perovskite core-shell architectures. Despite the need for further optimization, we are confident that our approach can be extended to thin film architectures, and more efficient Cs-based LEDs of enhanced stability are feasible.

ASSOCIATED CONTENT

Supporting Information.

Experimental details, X-ray diffractograms, PL, absorbance, and time-resolved PL spectra (pdf).

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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REFERENCES

- (1) Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G. Perovskite Materials for Light-Emitting Diodes and Lasers *Adv. Mater.* **2016**, *28*, 6804-6834.
- (2) Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I. Properties and potential optoelectronic applications of lead halide perovskite nanocrystals *Science* **2017**, *358*, 745-750.
- (3) Kim, Y.-H.; Cho, H.; Lee, T.-W. Metal halide perovskite light emitters *Proceedings of the National Academy of Sciences* **2016**, *113*, 11694-11702.
- (4) Cho, H.; Jeong, S.-H.; Park, M.-H.; Kim, Y.-H.; Wolf, C.; Lee, C.-L.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S., et al. Overcoming the electroluminescence efficiency limitations of perovskite light-emitting diodes *Science* **2015**, *350*, 1222-1225.
- (5) Quan, L. N.; Zhao, Y.; Garcia de Arquer, F. P.; Sabatini, R.; Walters, G.; Voznyy, O.; Comin, R.; Li, Y.; Fan, J. Z.; Tan, H., et al. Tailoring the Energy Landscape in Quasi-2D Halide Perovskites Enables Efficient Green-Light Emission *Nano Lett.* **2017**.
- (6) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , $\text{X} = \text{Cl}$, Br , and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut *Nano Lett.* **2015**, *15*, 3692-3696.
- (7) Pan, A.; He, B.; Fan, X.; Liu, Z.; Urban, J. J.; Alivisatos, A. P.; He, L.; Liu, Y. Insight into the Ligand-Mediated Synthesis of Colloidal CsPbBr_3 Perovskite Nanocrystals: The Role of Organic Acid, Base, and Cesium Precursors *ACS Nano* **2016**, *10*, 7943-7954.

- (8) Li, J.; Xu, L.; Wang, T.; Song, J.; Chen, J.; Xue, J.; Dong, Y.; Cai, B.; Shan, Q.; Han, B., et al. 50-Fold EQE Improvement up to 6.27% of Solution-Processed All-Inorganic Perovskite CsPbBr₃ QLEDs via Surface Ligand Density Control *Adv. Mater.* **2016**, *29*, 1603885.
- (9) Liang, Z.; Zhao, S.; Xu, Z.; Qiao, B.; Song, P.; Gao, D.; Xu, X. Shape-Controlled Synthesis of All-Inorganic CsPbBr₃ Perovskite Nanocrystals with Bright Blue Emission *ACS Appl. Mater. Interfaces* **2016**, *8*, 28824-28830.
- (10) Huang, H.; Lin, H.; Kershaw, S. V.; Susha, A. S.; Choy, W. C. H.; Rogach, A. L. Polyhedral Oligomeric Silsesquioxane Enhances the Brightness of Perovskite Nanocrystal-Based Green Light-Emitting Devices *J. Phys. Chem. Lett.* **2016**, *7*, 4398-4404.
- (11) Li, G.; Rivarola, F. W. R.; Davis, N. J. L. K.; Bai, S.; Jellicoe, T. C.; de la Peña, F.; Hou, S.; Ducati, C.; Gao, F.; Friend, R. H., et al. Highly Efficient Perovskite Nanocrystal Light-Emitting Diodes Enabled by a Universal Crosslinking Method *Adv. Mater.* **2016**, *28*, 3528-3534.
- (12) Pan, J.; Quan, L. N.; Zhao, Y.; Peng, W.; Murali, B.; Sarmah, S. P.; Yuan, M.; Sinatra, L.; Alyami, N. M.; Liu, J., et al. Highly Efficient Perovskite-Quantum-Dot Light-Emitting Diodes by Surface Engineering *Adv. Mater.* **2016**, *28*, 8718-8725.
- (13) Zhang, X.; Xu, B.; Zhang, J.; Gao, Y.; Zheng, Y.; Wang, K.; Sun, X. W. All-Inorganic Perovskite Nanocrystals for High-Efficiency Light Emitting Diodes: Dual-Phase CsPbBr₃-CsPb₂Br₅ Composites *Adv. Funct. Mater.* **2016**, *26*, 4595-4600.
- (14) Li, X.; Wu, Y.; Zhang, S.; Cai, B.; Gu, Y.; Song, J.; Zeng, H. CsPbX₃ Quantum Dots for Lighting and Displays: Room-Temperature Synthesis, Photoluminescence Superiorities, Underlying Origins and White Light-Emitting Diodes *Adv. Funct. Mater.* **2016**, *26*, 2435-2445.
- (15) Akkerman, Q. A.; Gandini, M.; Di Stasio, F.; Rastogi, P.; Palazon, F.; Bertoni, G.; Ball, J. M.; Prato, M.; Petrozza, A.; Manna, L. Strongly emissive perovskite nanocrystal inks for high-voltage solar cells *Nat. Energy* **2016**, *2*, 16194.
- (16) Sun, S.; Yuan, D.; Xu, Y.; Wang, A.; Deng, Z. Ligand-Mediated Synthesis of Shape-Controlled Cesium Lead Halide Perovskite Nanocrystals via Reprecipitation Process at Room Temperature *ACS Nano* **2016**, *10*, 3648-3657.
- (17) Seth, S.; Samanta, A. A Facile Methodology for Engineering the Morphology of CsPbX₃ Perovskite Nanocrystals under Ambient Condition *Sci. Rep.* **2016**, *6*, 37693.

- (18) Wei, S.; Yang, Y.; Kang, X.; Wang, L.; Huang, L.; Pan, D. Room-temperature and gram-scale synthesis of CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals with 50-85% photoluminescence quantum yields *Chem. Commun.* **2016**, 52, 7265-7268.
- (19) Zhang, F.; Zhong, H.; Chen, C.; Wu, X. G.; Hu, X.; Huang, H.; Han, J.; Zou, B.; Dong, Y. Brightly luminescent and color-tunable colloidal CH₃NH₃PbX₃ (X = Br, I, Cl) quantum dots: Potential alternatives for display technology *ACS Nano* **2015**, 9, 4533-4542.
- (20) Criss, C. M.; Luksha, E. Thermodynamic properties of nonaqueous solutions. IV. Free energies and entropies of solvation of some alkali metal halides in N,N-dimethylformamide *J. Phys. Chem.* **1968**, 72, 2966-2970.
- (21) Izatt, R. M. Charles J. Pedersen's legacy to chemistry *Chem. Soc. Rev.* **2017**, 46, 2380-2384.
- (22) Li, J.; Yim, D.; Jang, W. D.; Yoon, J. Recent progress in the design and applications of fluorescence probes containing crown ethers *Chem. Soc. Rev.* **2017**, 46, 2437-2458.
- (23) Kimura, K.; Kitazawa, S.; Maeda, T.; Shono, T. Cation-binding properties of poly- and bis(benzo-21-crown-7)derivatives *Fresenius' Z. Anal. Chem.* **1982**, 313, 132-136.
- (24) Cottingham, P.; Brutchey, R. L. On the crystal structure of colloiddally prepared CsPbBr₃ quantum dots *Chem. Commun.* **2016**, 52, 5246-5249.
- (25) Bhaumik, S.; Veldhuis, S. A.; Ng, Y. F.; Li, M.; Muduli, S. K.; Sum, T. C.; Damodaran, B.; Mhaisalkar, S.; Mathews, N. Highly stable, luminescent core-shell type methylammonium-octylammonium lead bromide layered perovskite nanoparticles *Chem. Commun.* **2016**, 52, 7118-7121.
- (26) Chen, W.; Bhaumik, S.; Veldhuis, S. A.; Xing, G.; Xu, Q.; Grätzel, M.; Mhaisalkar, S.; Mathews, N.; Sum, T. C. Giant five-photon absorption from multidimensional core-shell halide perovskite colloidal nanocrystals *Nat. Commun.* **2017**, 8, 15198.
- (27) De Roo, J.; Ibáñez, M.; Geiregat, P.; Nedelcu, G.; Walravens, W.; Maes, J.; Martins, J. C.; Van Driessche, I.; Kovalenko, M. V.; Hens, Z. Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals *ACS Nano* **2016**, 10, 2071-2081.
- (28) Zou, S.; Liu, Y.; Li, J.; Liu, C.; Feng, R.; Jiang, F.; Li, Y.; Song, J.; Zeng, H.; Hong, M., et al. Stabilizing Cesium Lead Halide Perovskite Lattice through Mn(II) Substitution for Air-Stable Light-Emitting Diodes *J. Am. Chem. Soc.* **2017**, 139, 11443-11450.

- (29) Song, J.; Li, J.; Li, X.; Xu, L.; Dong, Y.; Zeng, H. Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX₃) *Adv. Mater.* **2015**, *27*, 7162–7167.
- (30) Xu, F.; Ma, X.; Haughn, C. R.; Benavides, J.; Doty, M. F.; Cloutier, S. G. Efficient Exciton Funneling in Cascaded PbS Quantum Dot Superstructures *ACS Nano* **2011**, *5*, 9950–9957.
- (31) Kim, Y.-H.; Lee, G.-H.; Kim, Y.-T.; Wolf, C.; Yun, H. J.; Kwon, W.; Park, C. G.; Lee, T. W. High efficiency perovskite light-emitting diodes of ligand-engineered colloidal formamidinium lead bromide nanoparticles *Nano Energy* **2017**, *38*, 51–58.
- (32) Kim, Y.-H.; Wolf, C.; Kim, Y.-T.; Cho, H.; Kwon, W.; Do, S.; Sadhanala, A.; Park, C. G.; Rhee, S.-W.; Im, S. H., et al. Highly Efficient Light-Emitting Diodes of Colloidal Metal–Halide Perovskite Nanocrystals beyond Quantum Size *ACS Nano* **2017**, *11*, 6586–6593.
- (33) Xing, J.; Yan, F.; Zhao, Y.; Chen, S.; Yu, H.; Zhang, Q.; Zeng, R.; Demir, H. V.; Sun, X.; Huan, A., et al. High-Efficiency Light-Emitting Diodes of Organometal Halide Perovskite Amorphous Nanoparticles *ACS Nano* **2016**, *10*, 6623–6630.