1. Materials and synthetic procedures

1.1 Materials

Oleic acid (OLA, 90% technical grade, Aldrich), hexylamine (C6, 99%, Aldrich), octylamine (C8, 99%, Aldrich), n-decylamine (C10, 99%, Acros Organics), dodecylamine (C12, 98% Acros Organics), 1-tetradecylamine (C14, 98%, Aldrich), and 1-hexadecylamine (C16, 90%, Alfa Aesar), lead (II) bromide (PbBr₂, 98%, Acros Organics), toluene (99.8%, Fisher Chemical), tert-butyl alcohol (t-BuOH, for analysis, Fisher Chemical), N,N-dimethylformamide (DMF, >99.8%, Aldrich), Ethanol (EtOH, absolute for analysis, Merck), hydrobromic acid (HBr, 48% in water, Sigma-Aldrich), methylamine (33% in absolute ethanol, Acros Organics), formamidine acetate (99%, Acros Organics), diethyl ether (>99.8%, Thommen-Furler AG). All chemicals listed above were used without any further treatment.

1.2 Synthesis of MABr and FABr precursors
Methylammonium bromide (MABr) was synthesized using the synthetic procedure reported by Pathak et al.\textsuperscript{1} MABr was synthesized by mixing 10 mL of methylamine (33% in EtOH) with 7.5 mL of HBr (48% in H\textsubscript{2}O) in 100 mL EtOH. The reaction mixture was stirred for 60 min under ambient conditions and followed by removal of the solvent at 60 °C by means of rotary evaporator. Formamidinium bromide (FABr) was synthesized according to the synthetic route developed by Eperon et al.\textsuperscript{2} Formamidine acetate was dissolved in 2 molar equivalents of HBr (48% in H\textsubscript{2}O) and left under stirring for 10 min. at 50 °C. The solvent was removed at 100 °C by means of rotary evaporator. The resulting solid was washed several times with diethylether and recrystallized with EtOH followed by drying in vacuum oven at 60 °C.

1.3 Synthesis of perovskite nanocrystals
The colloidal perovskite nanocrystals, FA\textsubscript{0.5}MA\textsubscript{0.5}PbBr\textsubscript{3} were synthesized using modified synthetic route reported in our earlier report\textsuperscript{3}. Firstly, the FABr and MABr (0.53 M) precursors were distinctly dissolved in ethanol, while PbBr\textsubscript{2} (0.4 M) was dissolved in polar N,N-dimethylformamide (DMF) solvent. The OLA (625 µL) and x ligand (where x: hexylamine (20 µL) or octylamine (25 µL) or decylamine (30 µL) or dodecylamine (35 µL) or tetradecylamine (32.2 µL) or hexadecylamine (36.4 µL), were consecutively mixed with non-polar solvent (Toluene, 12.5 mL) stirring in round bottle (RB) flask. Later, PbBr\textsubscript{2} precursor was mixed dropwise in the RB. The FABr and MABr precursor solutions were premixed in the ratio of 1:1 before final reaction. Subsequently, the precursor solutions mentioned above were added dropwise (375 µL of FA/MA stoichiometric solution and 625 µL of PbBr\textsubscript{2}) to a non-polar toluene solution consisting long chain organic surfactants, OA as long chain ligand and OLA as stabilizer under constant stirring. An instantaneous colloidal crystallization is triggered due to poor solubility of perovskite precursors in nonpolar toluene. Upon centrifugation at 8000 rpm for 8 min, the reaction mixture is separated in supernatant and precipitate. The resultant supernatant is discarded and the precipitate containing perovskite nanocrystals is redispersed in 2.5 mL of fresh toluene. Finally, the colloidal dispersion was centrifuged again and filtered through a 0.2 µm pore size filter to separate the supernatant, which was used as the final colloidal dispersion.

2. Morphological characterizations
Transmission electron microscopy (TEM) images of perovskite nanocrystals with various type of ligands were collected in cryogenic conditions using STEM (Hitachi HD 2700) equipped with cryo-holder (liquid nitrogen) with high beam acceleration voltages from 80 to 200 kV. Room temperature TEM images were acquired using Titan Krios FEG TEM.

3. Photophysical characterizations
3.1 Absorption spectra of perovskite NC solids were measured using a JASCO V670 spectrometer.
3.2 Photoluminescence (PL) spectra and absolute PLQY were recorded with Hamamatsu CCD spectrometer (wavelength resolution < 2 nm). The absolute PLQYs in colloidal solutions (in toluene) and spin-casted thin films were determined using the Quantaurus QY (C11347-11) from Hamamatsu equipped with 150 W xenon light source and a 3.3 inches integrating sphere, which is coated with highly reflective Spectralon.
3.3 Time resolved photoluminescence (TRPL) spectra of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ perovskite nanocrystal solids with varying the hydrophobic chain length of alkylamine ligands, C$_6$, C$_8$, C$_{10}$, C$_{12}$, C$_{14}$, and C$_{16}$, a regular interval of 0.2, were performed using a Hamamatsu Quantaurus-Tau (Q-tau) Fluorescence Lifetime Spectrometer (C11367-31) equipped with a photon counting measurement system. The samples were exited using a 365 nm pulsed emission with a repetition rate of 200 kHz and 10000 counts.

4. X-rays diffraction (XRD)
XRD patterns of 2D perovskites were collected using a PANalytical X’Pert PRO-MPD diffractometer with Cu-Kα radiation. The data were recorded in the range of 10-70° 2θ at room temperature with an angular step size of 0.05° and a counting time of 0.23 seconds per step.

5. Optical characterizations
The psi (ψ) and delta (Δ) plots of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ thin films with different ligands were acquired through a micro-spot Ellipsometer from SENTECH SE850 at an incidence angle of 70°. The resulting data were processed using the Sellmeier function to obtain the refractive indices ($n$) and thicknesses of samples. On the contrary, the $k$ values of samples remained zero as the lambda (λ) vs angle ψ and Δ functions were fitted in the non-absorbing reason (transparent reason). The empirical relationship between refractive index and wavelength for a specific transparent medium.

\[
n^2(\lambda) = 1 + \sum_i \frac{A_i \lambda^2}{\lambda^2 - B_i}
\]

5.1 Orientation of PL transition dipole moment and momentum-resolved (k-space) PL emission

The angle dependent photoluminescence (PL) of all samples are characterize using a commercial Phelos instrument (Fluxim Inc.) equipped with a CCD spectrometer and a polarizer with a hemisphere glass lens. This feature allows the extraction of photons with a normalized wave vector $k/k_0 > 1$, usually lost in substrate modes. First, the colloidal solutions of perovskite samples were spin-casted on the glass substrates. Then, the substrate was placed on the top of the hemispherical glass lens using a refractive index matching oil. The latter ensures a lack of air in the substrate-lens interface. A typical measurement procedure consisted of simultaneous sweeping both polarization (0) and viewing angles (φ). The PL emission is measured at different angles by varying the viewing angle from 0° to 85°, in the steps of 5°, whereas the polarizer angle was varied between 0° to 90° with the step size of 10°, where 0° corresponds to p- and 0° = 90° to s-polarization. Later on, a LED head emitting light was mounted on top and a 3 x 5 mm$^2$ wide spot of the sample was excited with an intensity of approximately $30 \pm 5$ W m$^{-2}$. The thin film samples were then excited with typical ultraviolet LED having an emission maximum of 275 nm at a fixed incident angle of 45°.

All measured emission patterns were converted to k-space. For each polarization angle, the relation $I(\varphi)$ vs. $\varphi$, which is obtained experimentally, can be transformed into $I(k/k_0)$ vs. $k/k_0$ using the following relations:

\[
\begin{align*}
n^2(\lambda) &= 1 + \frac{A_1 \lambda^2}{\lambda^2 - B_1} + \frac{A_2 \lambda^2}{\lambda^2 - B_2} + \frac{A_3 \lambda^2}{\lambda^2 - B_3} \\
I(k/k_0) &= I(\varphi) \times \frac{k_0^2}{k^2}
\end{align*}
\]
\[ \frac{k_x}{k_0} = n_{\text{sub}} \cdot \sin \varphi \cdot \cos \theta \]  
\[ \frac{k_y}{k_0} = n_{\text{sub}} \cdot \sin \varphi \cdot \sin \theta \]  
\[ I(k/k_0) = \frac{I(\varphi, \theta)}{\cos \varphi} \cdot C \]

where \( k/k_0 \) and \( n_{\text{sub}} \) represent the normalized wave vector and substrate refractive index \( n \), respectively. \( C \) equals to \( \sqrt{\varepsilon \cdot \omega \cdot c} \), with \( \varepsilon \) being the permeability of the glass substrate at the emission frequency \( \omega \). We assumed the emission width to be a constant. Furthermore, in most of the cases shown in this work, all intensities were normalized and therefore a quantitative determination of \( C \) was not necessary. As a result, all transformed data could be plotted as 2D contour plots, thus generating \( k \)-space radiation patterns. These were then compared to theoretically predicted ones.

The experimental data was evaluated with the computation software Setfos provided by Fluxim Inc. A precise film thickness \( t \) as well as a relation between emitter \( n \) value and incident light wavelength \( \lambda \) were obtained by means of SE and used as input parameters for the optical model. We assumed the dispersion of \( n \) value with respect to \( \lambda \) is considered. Setfos allows to compute the coherent light propagation in individual optical layers/cavities as well as across multilayer stacks by considering the respective polarization-dependent Fresnel reflection and transmission coefficients at each of the interfaces.\(^5\) Light generation inside an active layer is described as power radiated by spatially distributed electrical dipoles (dipole moment \( \vec{p} \))\(^7\)\(^-\)\(^9\). Here, Setfos was used to simulate the angle-dependent \( s \) - and \( p \)-polarized PL intensity, \( I_p(\varphi) \) and \( I_s(\varphi) \), from the perovskite NC solids sample attached to the hemispherical glass lens, for the given input parameters \( t, n_{\text{SL}}(\lambda) \). The only fitting parameter, namely the emission dipole orientation

\[ R_{IP} = \frac{\Sigma p_x^2 + p_y^2}{\Sigma p_z^2} \]

representing the fraction of in-plane oriented dipoles, was determined by fitting of \( p \)-polarized emission \( I_p \) as a function of \( \varphi \). Based on the computed \( R_{IP} \) and other input parameters, the \( s \)-polarized emission \( I_s \) was calculated afterwards and compared to experimental data.

For the sake of comparability with the measurement, the simulated emission patterns for polarization angles \( 0^\circ < \theta < 90^\circ \) were calculated as a superposition of \( I_p(\varphi) \) and \( I_s(\varphi) \),

\[ I(\theta, \varphi) = I_p(\varphi) \cdot (\cos \theta)^2 + I_s(\varphi) \cdot (\sin \theta)^2. \]

Finally, all computed \( I(\theta, \varphi) \) were treated analogously to experimental data, using equations (1) – (3).

5.2 Optical simulations for light out-coupling

The light out-coupling in the optimized perovskite LED device was computed using a commercial software programme Setfos 4.6 from Fluxim Inc. The device layer sequence of
ITO; 120 nm) / PEDOT:PSS (32 nm) / perovskite NC film (15 - 30 nm) / 3TPYMB (45 nm) / LiF (1 nm) / Al (70 nm) was utilized for computations, while the ETL thickness also varied between 5 to 200 nm. The experimental characteristics such as refractive index (n), individual layer thickness, photoluminescence spectra, orientation of emission dipole moment (Θ) of NC solids, and recombination profile considered as Gaussian distribution were independently characterized to simulate the amount of out-coupled light and various mode of losses, including substrate, absorption, waveguide, and evanescent losses, by varying the emission layers or ETL thicknesses. The simulated out-coupling efficiencies of perovskite LEDs were computed using a commercial software program Setfos 4.6 from Fluxim Inc. by varying the emissive layer thicknesses from 5 nm to 80 nm. Particularly, we have not observed any significant change in the out-coupling efficiencies of devices (Fig. S12) within the EML thickness range of 15-30 nm. Note that the EML range was mentioned for all six samples. The thickness of each sample varies within the above range even if they have similar concentrations of perovskite NCs in colloidal solutions.

6. Materials, fabrication and characterizations of PeLEDs

6.1 Materials
Patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω/□ and a size of 3 × 3 cm² were purchased from Lumtech Corp. The hole injection material poly(3,4-ethylene-dioxythiophene)-poly(styrene sulfonate) (PEDOT: PSS) was procured from Heraeus (Clevios AI 4083). The electron transporting material tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB) and 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PQT2T) are procured from Lumtech Corp. The electron injection material lithium fluoride (LiF) (99.98%) is purchased from Acros Organics. Aluminum (Al) pellets (99.999%) were purchased from Kurt J. Lesker Co. Ltd. All materials were used without any further purification.

6.2 Fabrication of perovskite LEDs
Patterned ITO coated glass substrates were sonicated in the Extran MA02 neutral detergent and deionized (DI) water mixture (1:3). Afterward, these substrates were sequentially sonicated in DI water, acetone, and isopropanol, each for 10 minutes. The substrates were then exposed to oxygen plasma for 10 min in diener plasma cleaner. Thereafter, the aqueous PEDOT: PSS solution was spin-coated on the pre-cleaned ITO glass at a spin speed of 4000 rpm for 50 s. All substrates were then transported to nitrogen atmosphere glovebox. These substrates were annealed at 130 °C for 0.5 h in the glovebox. Then successive layers were deposited through spin-casting and thermal evaporation, respectively. Before spin-casting, the nanocrystals were synthesized with six different ligands, hexylamine (C6), octylamine (C8), decylamine (C10), dodecylamine (C12), tetradecylamine (C14), and hexadecylamine (C16), for emissive layer (EML). The concentration of colloidal solutions was maintained at 7 ± 1 mg ml⁻¹ in toluene through maintaining their absorption coefficient. The EML was deposited at a spin rate of 2500 rpm for 40 s through spin-casting. All substrates were mounted on a substrate holder, which is then transferred into an ultrahigh vacuum evaporation chamber. Consequently, a 45 nm ETL was deposited on the EML by the thermal evaporation. Lastly, a 1 nm LiF electron injection layer and a 70 nm Al cathode layer were also deposited in a high vacuum chamber (8 × 10⁻⁸ mbar) by using a shadow mask. Each substrate is patterned to realize four devices, each with an active area of 25 mm² as defined by the overlapping area of the bottom ITO anode and top Al cathode layers. Finally, these devices were stored in the glove box and characterized in the
ambient atmosphere with a room temperature 25 ±5 °C and relative humidity ( RH = 30 – 50%). The electrical stability of NC LED device is measured using PO-T2T as additional electron transporting layer.

6.3 Characterization of perovskite LEDs

Current density-voltage-luminance (J-V-L) characteristics of the perovskite LEDs were measured using a Photo Research PR 655 SpectraScan spectrometer and Keithley 2400 source meter. The electroluminescence (EL) spectra of all the devices were also recorded by using a PR 655 spectrometer. The $\eta_{\text{ext}}$ was calculated as the total number of emitted photons divided by the total number of injected electrons by assuming a Lambertian-type emission pattern. Moreover, the angular EL emission of devices were also characterized by the Phelos (Fluxim Inc.) angle dependent measurement set-up to calculate the $\eta_{\text{ext}}$ of LEDs with external light outcoupling technique.

### Table

**Table S1.** Electroluminescence characteristics of the FA$_{0.5}$MA$_{0.5}$PbBr$_3$ perovskite NCs by varying the alkyl chain length from C6 to C16 in the alkylamine ligand.

| a) Alkyl chain length | b) $V_{\text{on}}$ | $\eta_{\text{CE}}$ (cd A$^{-1}$) | $\eta_{\text{ext}}$ (%) | $\eta_{\text{PE}}$ (lm W$^{-1}$) | $\lambda_{\text{max}}$ (nm) | $L_{\text{max}}$ (cd m$^{-2}$) |
|----------------------|-------------------|-------------------------------|------------------------|-------------------------------|---------------------------|-------------------------------|
| C6                   | 3.00              | 18.33                         | 3.78                   | 16.44                         | 528                       | 9555                          |
| C8                   | 3.04              | 28.54                         | 6.65                   | 25.62                         | 528                       | 9750                          |
| C10                  | 3.37              | 38.10                         | 9.91                   | 35.57                         | 528                       | 3322                          |
| C12                  | 3.67              | 27.08                         | 6.78                   | 24.31                         | 524                       | 805                           |
| C14                  | 4.28              | 0.49                          | 0.18                   | 0.38                          | 512                       | 2.45                          |
| C16                  | 4.32              | 0.39                          | 0.13                   | 0.31                          | 512                       | 2.46                          |

a) alkyl chain length in the alkylamine ligands used for the passivation of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ NCs. b) turn-on voltage of devices at an operating current density of 1 mA cm$^{-2}$. 

S6
Figures

**Figure S1.** (a) AFM topography of decylamine capped FA$_{0.5}$MA$_{0.5}$PbBr$_3$ perovskite nanocrystals and (b) thickness of single nanocrystal.

**Figure S2.** XRD patterns of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ perovskite nanocrystals by using aliphatic primary alkylamines type ligands with varying the alkyl chain length from C6 to C16.
**Figure S3.** Photophysical characteristics of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ with different ligands varying the alkyl chain from C6 to C16 (a) PL and absorbance spectra in toluene solution. (b) PL and absorbance spectra of thin-film samples.

**Figure S4.** PL spectra of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ NCs with varying the alkyl chain length in alkylamine ligands, (a) hexylamine (C6) and (b) hexadecylamine (C16) spin-coated thin films. The PL intensities were extracted from the PL spectra, which were recorded between 298 K and 77 K with a step size of 10 K.
Figure 5. Ambient $\eta_{PL}$ stability of colloidal solution of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ NCs with varying ligand length.
Figure S6 Time resolved PL spectra of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ NCs with varying the alkyl chain length from C6 to C16 in the alkylamine ligands, (a) hexylamine C6, (b) octylamine C8, (c) decylamine C10, (d) dodecylamine C12, (e) tetradecylamine C14, and (f) hexadecylamine C16 spin-coated thin films. The PL spectra of each thin film sample were collected between 298 K and 77 K.
Figure S7. Full width at half maximum (fwhm) of the PL spectra as a function of the temperature of NC samples capped with alkylamine ligand with varying the alkyl chain length from C6 to C16. The black solid line is the result of a fit using equation (1), including contributions from inhomogeneous broadening, acoustic phonons and optical phonons.
**Figure S8.** Experimental (exp.; top) and simulation (sim.; bottom) results of the average transition dipole moment vector \((k\text{-space})\) from the pattern of light emitted through a hemispherical glass lens (left). Comparison between experimental (circle) and simulated (line) \(s\)- and \(p\)-polarized emission profiles for in-plane and out-of-plane emission dipoles (right). (a) C8, (b) C10, (c) C12, (d) C14, and (e) C16.
\textbf{Figure S9.} The $n$ profile (figure on left side) of FA$_{0.5}$MA$_{0.5}$PbBr$_3$ perovskite NCs capped with alkylamine ligands varying the alkyl chain length (a) C6. (b) C8. (c) C10. (d) C12. (e) C14. and (f) C16.
Figure S10. Angular dependance of the polarized emission in the FA$_{0.5}$MA$_{0.5}$PbBr$_3$ perovskite NCs film by varying the alkyl chain length from C6 to C16, (a) hexylamine C6, (b) octylamine C8, (c) decylamine C10, (d) dodecylamine C12, (e) tetra-decylamine C14, and (f) hexadecylamine C16. The polarized emission was recorded by changing the polarizing angle from 0 to 90° with a step-size of 10° and stage angle from 0 to 85° with a step size of 5°.
Figure S11. Schematic device architecture of LEDs based on FA$_{0.5}$MA$_{0.5}$PbBr$_3$ NCs with varying the alkyl chain length from C6 to C16 in the alkylamine ligands.

Figure S12. Distributions of power fractions as a function of EML, FA$_{0.5}$MA$_{0.5}$PbBr$_3$ perovskite NCs film, thickness computed by optical simulation using a device architecture of ITO (120 nm)/PEDOT:PSS (35 nm)/EML (5 to 80 nm)/3TPYMB (35 nm)/LiF (1 nm)/Al (70 nm). The optical parameters such as refractive index and film thickness was characterized by ellipsometer, while the experimental EL spectra were also used for reference. The orientation emission dipole (Θ) was calculated through fitting experimental angle dependent PL with computational data.
Figure S13. External quantum efficiency ($\eta_{\text{ext}}$) distribution as a function of alkyl chain length varying from C6 to C16 in the alkylamine ligands.

Figure S14. SEM micrograph of decylamine (C10) capped FA$_{0.5}$MA$_{0.5}$PbBr$_3$ NCs emissive layer spin-coated on PEDOT:PSS layer.
Figure S15. Angle dependent EL of LEDs based on FA$_{0.5}$MA$_{0.5}$PbBr$_3$ perovskite NCs passivated with decylamine (C10) as ligand.

Figure S16. The EL spectra of device, at 5V, before and after electrical stress.
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