**Supplementary Information**

# Thiocarboxylic Acids for Robust Passivation and Advanced Applications of Perovskite Nanocrystals

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## Experimental Methods

### Materials

1-Adamantaneacetic acid (Ada-CA, >99.0%), lead (II) bromide ($PbBr_2$, >98.0%), formamidine acetate (FAAc, 99%), n-octanoic acid (OctA, >98.0%), zinc bromide ($ZnBr_2$, >98.0%), tetra-n-octylammonium bromide (TOAB, >98.0%) didecyldimethylammonium bromide (DDAB, >98.0%), and cyclopentyl methyl ether stabilized with BHT (CPME, 99.5%) were purchased from Tokyo Chemical Industry Co., Ltd. Ethyl acetate (EtOAc, 99.5%), toluene (99.5%), hydrochloric acid (35.0~37.0%) and dichloromethane (DCM, 99.5+%) were purchased from Wako Pure Chemical Co. (Osaka, Japan). Lawesson's reagent (90%), cesium acetate (CsAc, 99.9%), oleic acid (90%) was purchased from Sigma-Aldrich. Poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was purchased from Heraeus. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA, Mw ~128 kDa) was purchased from MS Solution. LiF and Al were purchased from iTASCO. CPME was purified by distillation, and all other chemicals were used without further purification.

**Synthesis of TCA**

The TCA was synthesized following the previous method with some modification.[1] The carboxylic acid precursor (1 mmol), Lawesson's reagent (0.75 mmol), and chlorobenzene (20 mL) were placed in a three-neck flask. The mixture was reacted at 120˚C for 6 h. After cooling to room temperature, 20 mL of 1M NaOH aq. was added to the mixture, and the mixture was stirred for 30 min. The crude solution was extracted with water and EtOAc to collect the aqueous phase. The aqueous phase was acidified to pH = 2.0 with hydrochloric acid. In addition, DCM was added to the mixture and the organic phase was collected. The solution was removed by a rotary evaporator, and the product was extracted with hexane and acetonitrile to collect the hexane. Finally, the hexane was removed by a rotary evaporator to obtain the product.

Adamantane thioacetic acid: $^{1}$H NMR (600 MHz, Chloroform-d, δ in ppm): 2.35 (s, 2H; $CH_2$), 1.95 (s, 3H; CH), 1.65 (m, 12H, $CH_2$). $^{13}$C NMR (150.9 MHz, Chloroform-d, δ in ppm): 56.5, 42.3, 36.6, 36.5, 34.3, 28.6

**Preparation of PeNCs and ligand exchange**

PeNCs were prepared based on the reported method with modifications. The PeNCs were prepared mixing the following solutions: Cs stock solution: 0.8 mmol of CsAc and 0.16 mmol of FAAc were dissolved in 7.1 mL of octanoic acid. Pb stock solution: 1 mmol of $PbBr_2$, 0.12 mmol of $ZnBr_2$, 3 mmol of TOAB were dissolved in 10 mL of toluene. DDAB stock solution: 0.26 mmol of DDAB were dissolved in 10 mL of toluene.

0.11 mL of Cs stock solution were injected into 1 mL of Pb stock solution under vigorous stirring. After 2 min reaction, 0.33 mL of DDAB stock solution was added. Furthermore, 2.9 mL of ethyl acetate was added, and the PeNCs were collected as a precipitate by centrifugation at 16,500 rpm for 1 min. The PeNCs were redispersed in 80 μL of 0.1 M Ada-TCA or Ada-CA/CPME solution. Additionally, 160 μL of EtOAc was added to the dispersion, and PeNCs were collected by centrifugation at 16,500 rpm for 1 min. Then, 500 μL of CPME

was added to the precipitates, and PeNCs were redispersed by ultrasonication. Finally, the aggregates were removed by centrifugation at 16,500 rpm for 1min and filtration with 0.2 μm PTFE filter.

**Fabrication of the LED device**

ITO-coated substrates were consecutively sonicated in acetone and 2-propanol for 15 min each and then treated with UV ozone. Poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-coated at 3,000 rpm for 60 s onto the ITO substrate and annealed at 150˚C for 30 min. Subsequently, 8 mg/mL solution of Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) in chlorobenzene was spin-coated at 3,000 rpm for 60 s onto the PEDOT:PSS layer and annealed at 120˚C for 20 min. As the emissive layer, PeNCs were spin-coated onto the PTAA layer in a nitrogen-filled glovebox. Subsequently, 40 nm of tris (1-phenyl-1H-benzimidazole) (TPBi), 1 nm of LiF, and 100 nm of aluminum were deposited by thermal evaporation under high vaccum (< $10^{-7}$ torr). The active area of the LED device was 0.06 $cm^2$. All devices were encapsulated using epoxy with a glass cover.

**Computational details**

Geometry optimization was carried out by the density functional theory (DFT) calculation at the B3LYP/6-31+G(d,p) level of theory.[2] Frequency calculations at the same level were performed to confirm that the optimized structures correspond to true minima (no imaginary frequencies). Electrostatic potential (ESP) maps and molecular volumes were obtained from the optimized electron densities using Gaussian 16.[3]

**Characterization**

PL spectra and PLQY were measured using a Jasco FP-8600 spectrometer. The PL lifetime was determined using a Hamamatsu C11367 Quantaurus-Tau instrument, and the PL decay curve was fitted using a biexponential function. Ultraviolet−visible absorption spectra (UV−vis) were measured by a Jasco V-670 spectrometer (detection wavelength range of 400–700 nm). Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDX) were measured by a JEOL JSM-IT800, accelerating voltage of 15 kV. The XRD patterns were obtained by a Rigaku SmartLab (diffractometer using Cu Kα radiation at 45 kV and 200 mA). The particle morphology and size distribution of the assemblies were obtained by TEM with a JEOL JEM-2100F (accelerating voltage of 200 kV) and dynamic light scattering (DLS) with a MICROTRAC NANOTRAC FLEX. $^{1}$H spectra were obtained by a JEOL JNM-EC500 instruments. Transient absorption spectra were obtained using the pump-probe technique (Helios, Ultrafast Systems). The output from a Ti:sapphire laser system (Spitfire, Spectra-Physics) was divided into two paths (800 nm, 80 fs, and 1 kHz). One path was frequency-doubled to serve as the pump beam, whereas the other was converted into a white light continuum for use as the probe beam. Both beams were focused onto the sample and the spectrum of the probe beam was obtained as a function of the delay time between the pump and probe beams. The electroluminescence efficiencies were obtained using a Keithley 2400 source measurement unit and Minolta CS-2000 spectroradiometer.

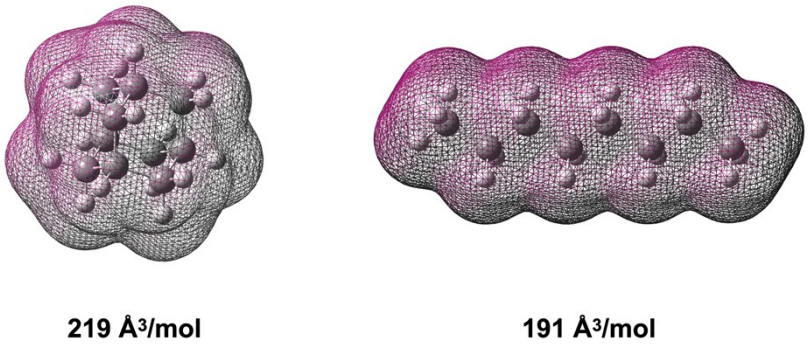


**Fig. S1** Calculated molecular volume of adamantane and octane by DFT calculation at B3LYP/6-31+G** level. The calculated volume is defined as the volume enclosed within a contour characterized by a density of 0.001 electrons/Bohr$^3$.

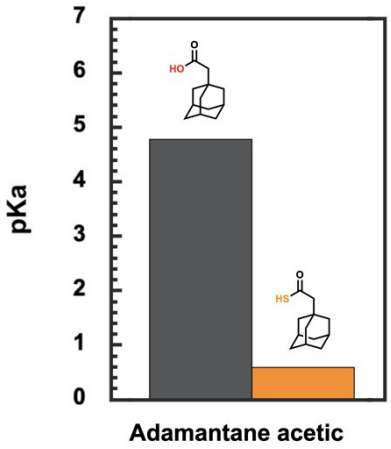


**Fig. S2** $pK_a$ estimation of Ada-CA and Ada-TCA. The $pK_a$ value were estimated by Marvinsketch ver.22. [4, 5]

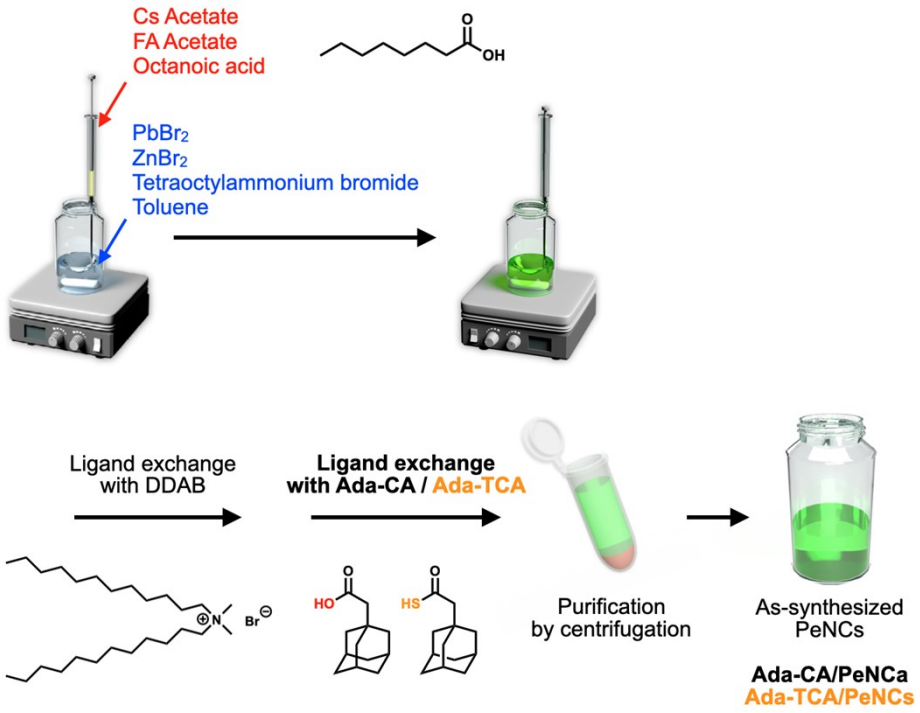


**Fig. S3** Schematic illustration of PeNCs preparation and ligand exchange process. The PeNCs were prepared following the reported methods with some modifications.[6]

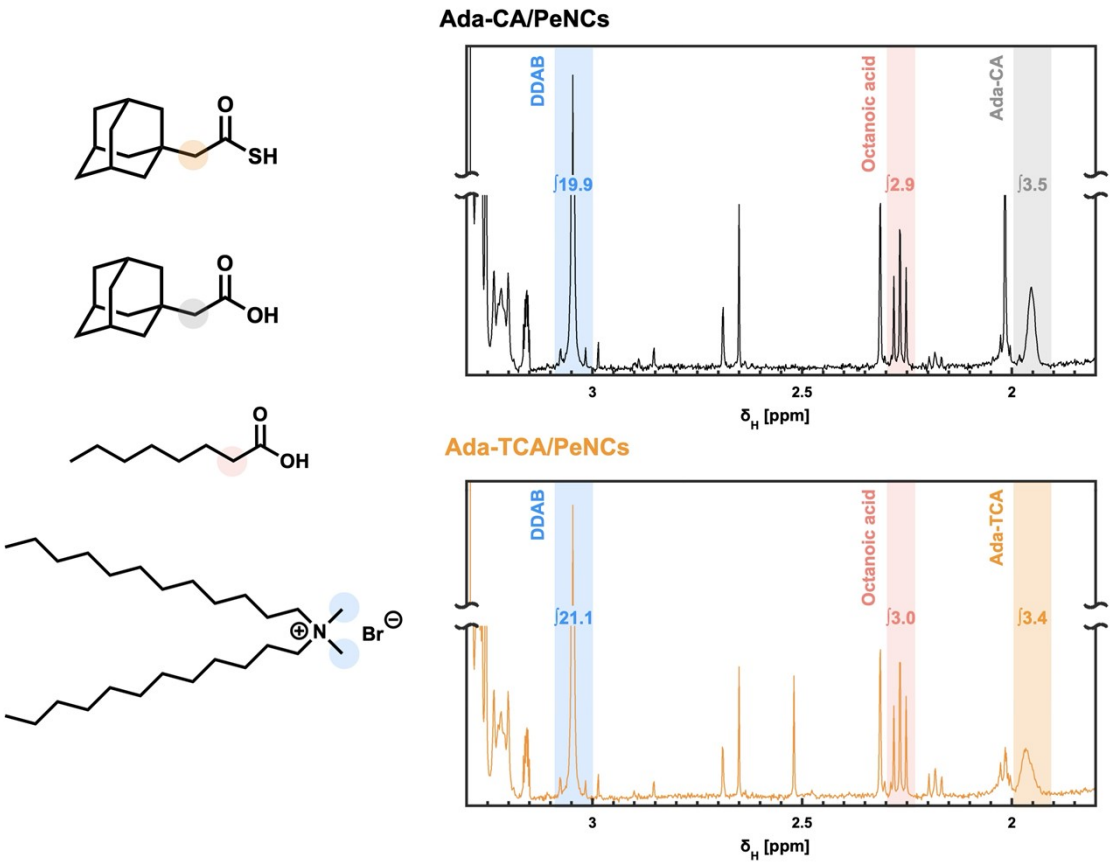


**Fig.S4** NMR spectra of Ada-CA/PeNCs and Ada-TCA/PeNCs. The ligand-specific peaks are highlighted, with the corresponding protons indicated by color coding in both the structural formula and the NMR spectrum. The $^{1}H$ NMR spectra were obtained in MeOH-$d_6$ to dissolve PeNCs at 500 MHz NMR.

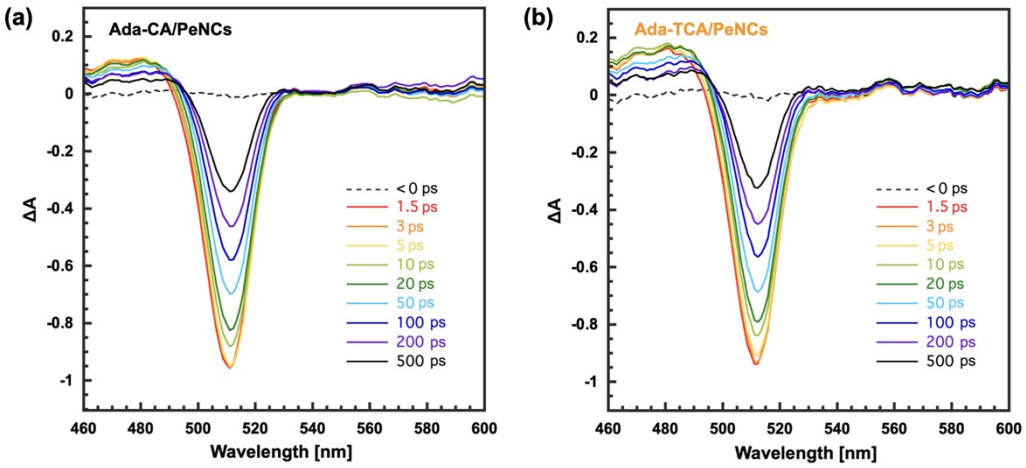


**Fig. S5** Transient absorption spectra of (a) Ada-CA/PeNCs and (b) Ada-TCA/PeNCs at different probe delay time.

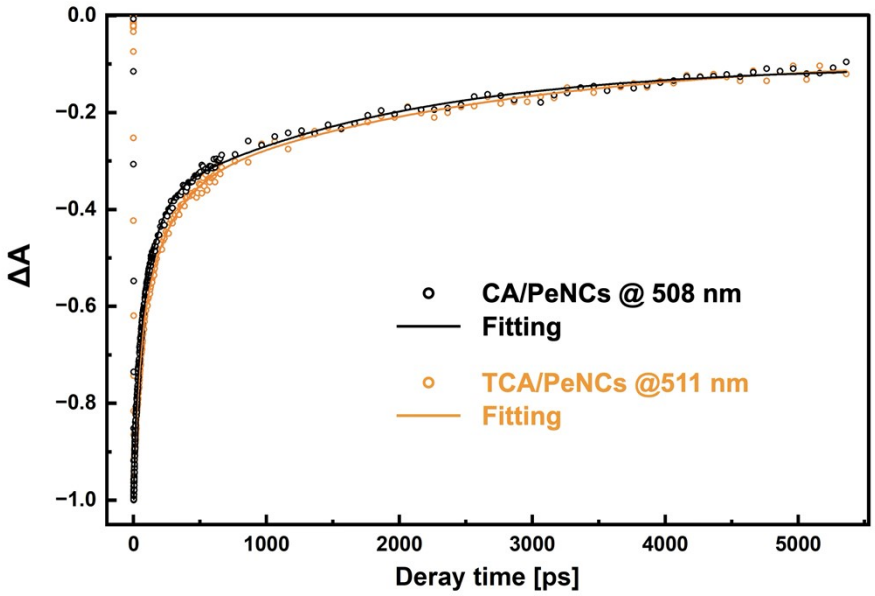


**Fig. S6** The bleach recovery dynamics for the PeNCs samples at the photo bleaching peak.

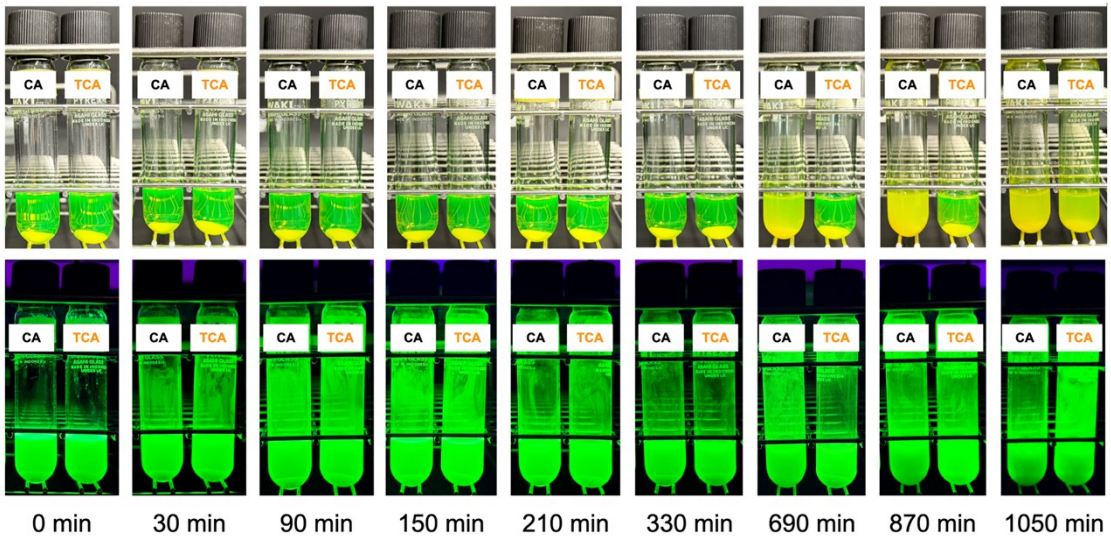


**Fig. S7** Sample images of Ada-CA/PeNCs and Ada-TCA/PeNCs during Thermal stability test under room light and 365 nm UV light.

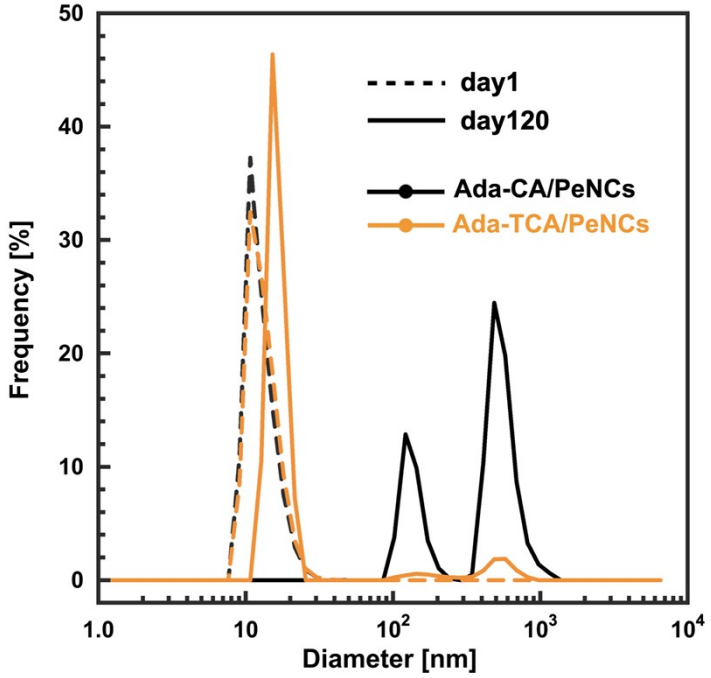


**Fig. S8** Particle size evolution measured by DLS during the shelf-life evaluation for 120 days

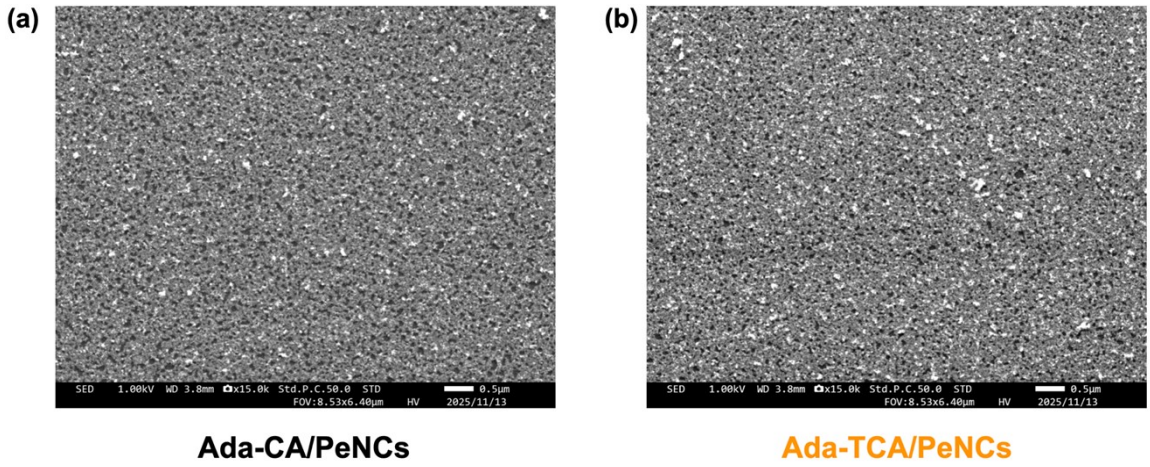


**Fig. S9** SEM image of (a) Ada-CA/PeNCs and (b) Ada-TCA/PeNCs thin film. The dark regions in the images correspond to the exposed substrate, and the pixel count of these areas was used to calculate the coverage of the PeNCs.

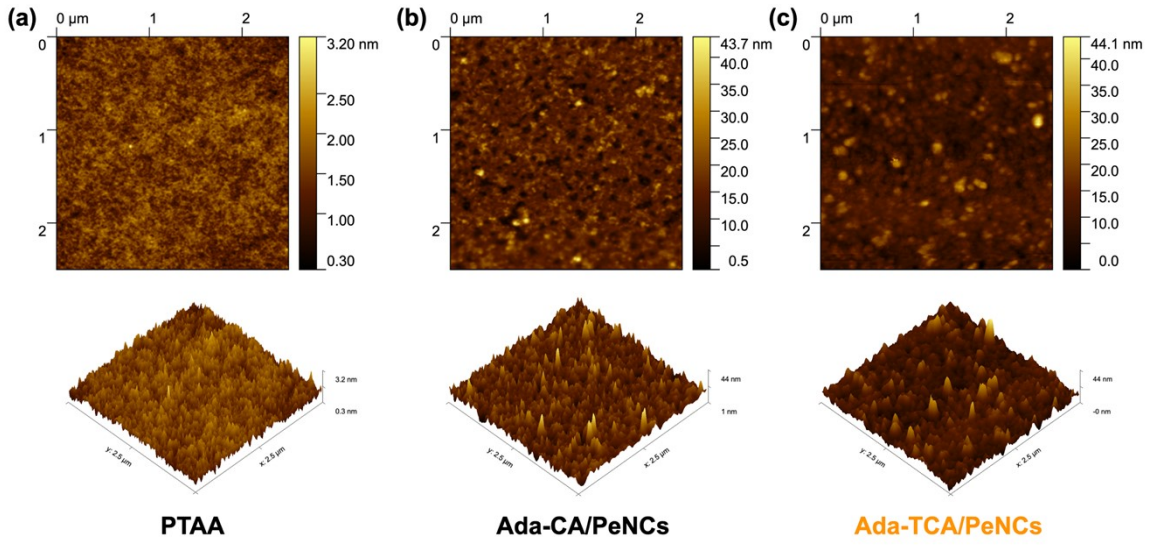


**Fig. S10** Top view and 3D view of AFM images of (a) PTAA (hole transport layer), (b) Ada-CA/PeNCs, and (c) Ada-TCA/PeNCs.

**Table S1** Surface ligands ratio of each PeNCs. These values were calculated from the integrated value of the spectral peaks measured by $^{1}$H NMR.

| Sample | DDAB [%] | Octanoic acid [%] | Ada-CA [%] | Ada-TCA [%] |
|---|---|---|---|---|
| Ada-CA/PeNCs | 56 | 24 | 20 | – |
| Ada-TCA/PeNCs | 57 | 24 | – | 18 |

**Table S2** The fitted constants ($A_1$ and $A_2$), average lifetimes ($\tau_{avg}$), and faster ($\tau_1$) and slower ($\tau_2$) decay times of the PeNCs are shown in Fig. 2(d).

| Sample | $\tau_1$ [ns] | $A_1$ | $\tau_2$ [ns] | $A_2$ | $\tau_{avg}$ [ns] |
|---|---|---|---|---|---|
| Ada-CA/PeNCs | 4.6 | 0.71 | 17.2 | 0.29 | 12.3 |
| Ada-TCA/PeNCs | 5.1 | 0.55 | 18.3 | 0.45 | 15 |

The TRPL decay curves obtained are shown in Fig. 2 (d) and were fitted with a biexponential function,

$$A(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 exp\left(-\frac{t}{\tau_2}\right)$$

where $A_1$ and $A_2$ are constant, t is time and $\tau_1$ and $\tau_2$ are the decay lifetimes, allowing for the determination of the nonradiative recombination ($\tau_1$) and radiative recombination ($\tau_2$) times. The average lifetime ($\tau_{avg}$) was calculated using following equation.

$$\tau_{avg} = \frac{A_1{\tau_1}^2 + A_2{\tau_2}^2}{A_1\tau_1 + A_2\tau_2}$$

**Table S3** The fitting parameters of bleaching recovery from transient absorption spectra in Fig. S6.

| Sample | $\tau_1$ [ns] | $A_1$ | $\tau_2$ [ns] | $A_2$ | $\tau_{avg}$ [ns] |
|---|---|---|---|---|---|
| Ada-CA/PeNCs | 4.6 | 0.71 | 17.2 | 0.29 | 12.3 |
| Ada-TCA/PeNCs | 5.1 | 0.55 | 18.3 | 0.45 | 15 |

**Table S4** Summary of RMS roughness value of the PeNCs thin films.

| Sample name | RMS [nm] |
|---|---|
| PTAA | 0.32 |
| CA/PeNCs | 4.1 |
| TCA/PeNCs | 3.7 |

**Table S5** Summary of LED performance, turn-on voltage at 1 $cd \cdot m^{-2}$ ($V_{ON}$), maximum current efficiency ($CE_{MAX}$), maximum luminance ($L_{MAX}$), and $EQE_{MAX}$.

| Entry | $V_{ON}$ @1$cd \cdot m^{-2}$ | $CE_{MAX}$ [$cd \cdot A^{-1}$] | $L_{MAX}$ [$cd \cdot m^{-2}$] | $EQE_{MAX}$ [%] |
|---|---|---|---|---|
| Ada-CA/PeNCs | 3.0 | 11.9 | 10,861 | 3.8 |
| Ada-TCA/PeNCs | 3.1 | 31.4 | 14,369 | 10.1 |

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