

Supplementary Information

Tailored Ligand Design Enabling Comprehensive Passivation of Perovskite Nanocrystals for Light-Emitting Diodes

*Taisei Kimura^a, Kenshin Yoshida^a, Kohei Narazaki^b, Kento Yanagihashi^b, Shun Hirashima^a,
Yua Oyama^a, Khadga S Thakuri^c, Yuta Ito^a, Satoshi Asakura^d, Motofumi Kashiwagi^e,
Matthew S White^{e, f}, Takayuki Chiba^{b, g}, and Akito Masuhara^{a, g*}*

- a. Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, Yamagata 992-8510, Japan
- b. Graduate School of Organic Material Science, Yamagata University, 4-3-16, Jonan, Yonezawa, Yamagata 992-8510, Japan
- c. Department of Physics, The University of Vermont, Burlington, Vermont 05405, USA
- d. ISE CHEMICALS Corporation, 1-3-1 Kyobashi, Chuo-ku, Tokyo, 104-0031, Japan.
- e. ZEON Corporation, 1-6-2 Marunouchi, Chiyoda-ku, Tokyo, 100-8246, Japan.
- f. Material Science Program, The University of Vermont, Burlington, Vermont 05405, USA
- g. Research Center for Organic Electronics (ROEL), Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata, 992-8510, Japan.

Synthetic Methods of Ligands

Materials

4-phenylbutyronitrile, phenylacetonitrile, and dimethyl carbonate (DMC, 98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Ammonia solution (2.0 M in methanol) was purchased from Sigma-Aldrich. Acetyl bromide (98.0%), ethanol (99.5%), ethyl acetate (EtOAc, 99.5%), hydrobromic acid (47.0 ~ 49.0%), and oleylamine were purchased from Wako Pure Chemical Co., Osaka, Japan. All reagents were used without any purification.

Synthesis of Oleylammonium Bromide (OAmBr)

30 mL of oleylamine and 100 mL of ethanol were placed in a flask, and the mixture was cooled in an ice bath. 18 mL of hydrobromic acid was dropwisely added to the flask under vigorous stirring. The mixture was reacted for 12 h at room temperature. After the reaction, most of the solvents were removed by rotary evaporator, and several volumes of EtOAc was added to the obtained mixture. The mixture was kept in the refrigerator for several hours. The solid components that precipitated are separated by centrifugation under appropriate conditions. The white solids were washed, frozen, and centrifuged for three times in the same way for purification. The final product was dried in a vacuum oven for overnight, and OAmBr was obtained.

Synthesis of Amidinium-Type Ligands (AmdBr-C2Ph and AmdBr-C4Ph)

Amidinium-type ligands were synthesized based on the Pinner reaction¹ with modifications. 30 mmol of nitrile compound (4-phenylbutyronitrile or phenylacetonitrile) and 21 mL of methanol were loaded into a three-neck flask and cooled in an ice bath under a nitrogen atmosphere. 240 mmol of acetyl bromide was added dropwise to the flask, and the mixture was stirred overnight at room temperature. After the reaction, most of the solvents were removed from the mixture by nitrogen gas flow. For the next reaction, 30 mL of ammonia solution was added to the crude

product and stirred for at least 12 h under an inert atmosphere. After the reaction had progressed sufficiently, the solvent was removed by rotary evaporator. The obtained solid was dissolved in a small amount of methanol and mixed in DMC for reprecipitation. The precipitation was carried out several times for purification. The final product was dried in a vacuum oven overnight, the amidinium-type ligand was obtained.

In this work, 4-phenylbutyronitrile or phenylacetonitrile was used as the nitrile compounds, and the synthesized ligands were labeled as AmdBr-C4Ph and AmdBr-C2Ph, respectively. ^1H NMR and ^{13}C NMR spectra were shown in Figure S1 and S2.

Experimental Methods

Materials

Lead (II) bromide (PbBr_2 , >98.0%), formamidine hydrobromide (FABr, 99.99%), N,N-dimethylformamide (DMF, 99.5%), dimethyl carbonate (DMC, 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%), methyl acetate (MeOAc, 98.0%), toluene (99.5%) were purchased from Wako Pure Chemical Co. (Osaka, Japan). Oleic acid (90%) was purchased from Sigma-Aldrich. CPME was purified with activated alumina to remove BHT, and all other chemicals were used without further purification.

Preparation of FAPbBr_3 PeNCs

220 mg of PbBr_2 , 75 mg of FABr, and 45.0 mg of OAmBr were dissolved in 1 mL of DMF to form a precursor solution. The precursor solution (900 μL) was injected into 15 mL EtOAc under vigorous stirring. The solution immediately turned a turbid yellowish-green color and was mixed for 3 min. The crude PeNCs were collected and centrifuged at 16,500 rpm for 3 min, and the supernatant was removed. The precipitate was added to 6 mL of cyclohexane and redispersed in the solvent. The dispersions were centrifuged again at 10,000 rpm for 1 min to collect the supernatants as pristine FAPbBr_3 PeNCs. Pristine FAPbBr_3 PeNCs were prepared at a concentration of $2 \text{ mg}\cdot\text{mL}^{-1}$ and used in the next step.

Preparation of Ligand Solution

0.4 mmol of AmdBr-C2Ph or AmdBr-C4Ph was added to 3 mL of tert-amyl alcohol. The ligand was completely dissolved by ultrasound irradiation.

Ligand Exchange and Purification/Concentration Process

250 μL of the ligand solution was added to 15 mL of the pristine PeNCs dispersion under vigorous stirring. To obtain OAmBr/PeNCs, tert-amyl alcohol, without any ligands, was added to the pristine PeNCs dispersion. The ligand exchange process lasted for 5 min. The same volume of DMC was added to the mixture, and the supernatant was removed by centrifugation at 16,500 rpm for 5 min. An equal volume of MeOAc was added directly to the precipitate, and the precipitate was dispersed by ultrasonication. The particles were collected via centrifugation at 16,500 rpm for 3 min. The purification process, which included redispersion in MeOAc and centrifugation, was repeated. An appropriate amount of CPME was added to the precipitate obtained after purification, and the large particles were removed by centrifugation at 10,000 rpm for 1 min. Finally, the PeNCs were filtered using a PTFE syringe filter and prepared to a concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$ for the fabrication of the LED devices.

Fabrication of the LED device

ITO substrates were washed with deionized water, spin-cleaned, and treated with UV ozone. Poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-coated onto the ITO substrate and annealed, resulting in a 40 nm thick layer. Subsequently, 4 mg/mL of poly-N-vinylcarbazole (PVK) in chlorobenzene was spin-coated onto the PEDOT:PSS layer and annealed, resulting in a 20 nm thick layer. As the emissive layer, PeNCs were spin-coated onto the PVK layer in a nitrogen-filled glovebox. Subsequently, tris (1-phenyl-1H-benzimidazole) (TPBi), lithium 8-quinolate (LiQ), and aluminum were deposited via thermal evaporation. The active area of the LED device is 0.04 cm^2 .

Characterization

PL spectra and PLQY were measured using a Jasco FP-8600 spectrometer. The PL lifetime was determined using a Hamamatsu C11367 QuantaTaurus-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). The FT-IR spectra were measured using Thermo Fisher Nicolet iS5 with iD5 ATR Accessory. Scanning Electron Microscope (SEM) were measured by a JEOL JSM-IT810, accelerating voltage of 10 kV. AFM images were obtained by Agilent 5500 SPM system. The XRD patterns were obtained by a Rigaku SmartLab (diffractometer using Cu K α radiation at 45 kV and 200 mA). The Halder–Wagner plots in this paper were generated using PDXL software (ver. 1.8.0.3) included with the system. 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. ^1H and ^{13}C NMR spectra were obtained by a JEOL JNM-EC500 and JNM-ECZ600R/M1 instruments. Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) conducted using a Thermo Fisher Scientific Theta probe with a He I ultraviolet source (21.22 eV) under a high vacuum of approximately 10^{-6} Pa. 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, 100 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. EL spectra were recorded using a Hamamatsu PMA-11 photonic multichannel analyzer. The current density–voltage and luminance–voltage characteristics were

measured with a Keithley 2400 source measure unit and a Minolta CS200 luminance meter, respectively.

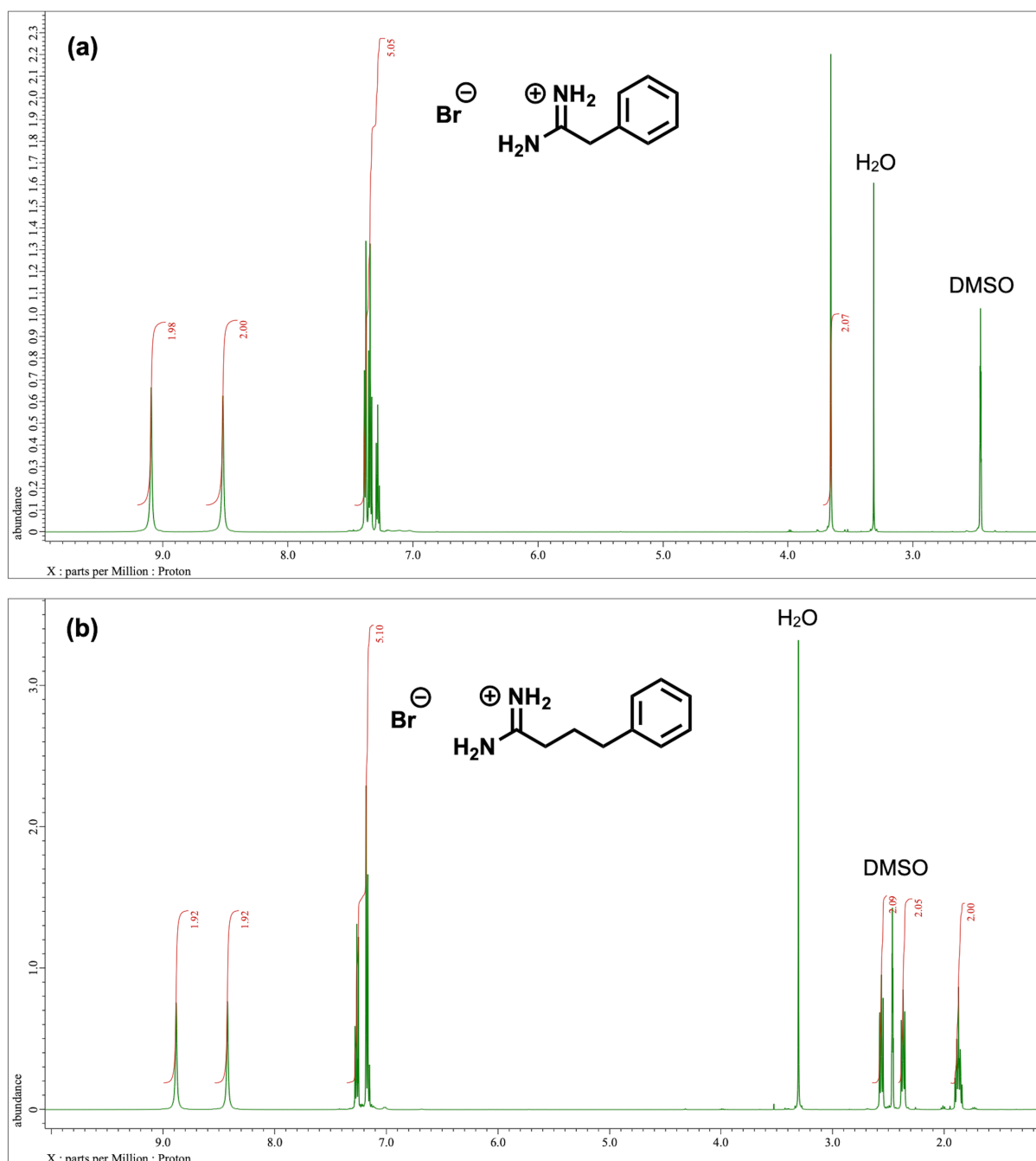


Fig. S1 ^1H NMR spectra of a) AmdBr-C2Ph and b) AmdBr-C4Ph. **AmdBr-C2Ph:** ^1H NMR (600 MHz, DMSO-d_6 , δ in ppm): 9.12 (s, 2H; NH_2), 8.55 (s, 2H; NH_2), 7.42-7.3 (m, 5H; Ar H), 3.69 (s, 2H; CH_2); **AmdBr-C4Ph:** ^1H NMR (600 MHz, DMSO-d_6 , δ in ppm): 8.92 (s, 2H; NH_2), 8.46 (s, 2H; NH_2), 7.28-7.15 (m, 5H; Ar H), 2.56 (t, $J = 9.3$ Hz, 2H; ArCH_2 -), 2.38 (t, $J = 9$ Hz, 2H; $\text{ArCH}_2\text{CH}_2\text{CH}_2$ -), 1.87 (tt, 2H, ArCH_2CH_2 -).

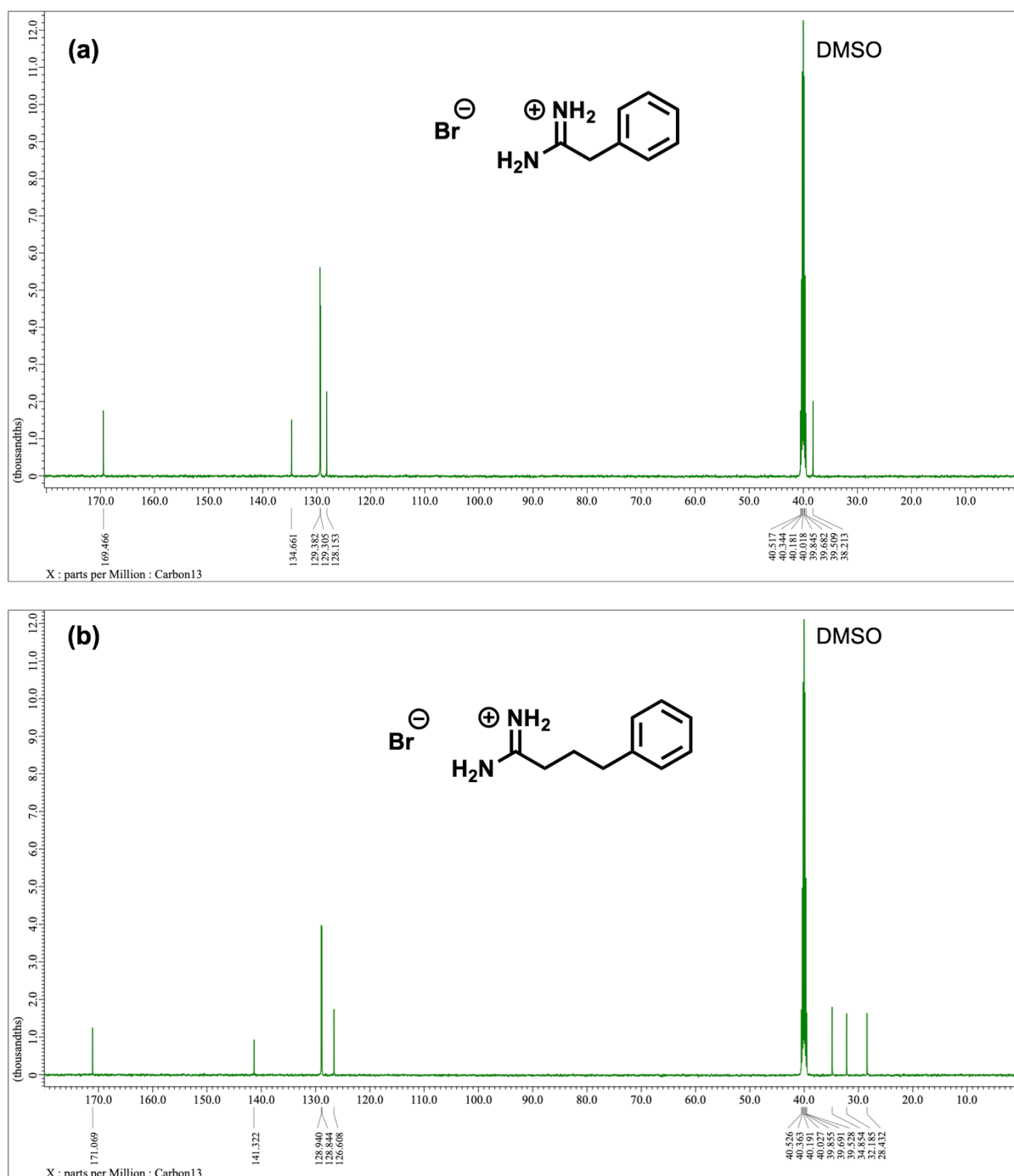


Fig. S2 ^{13}C NMR spectra of a) AmdBr-C2Ph and b) AmdBr-C4Ph. **AmdBr-C2Ph:** ^{13}C NMR (125 MHz, DMSO- d_6 , δ in ppm): 169.5, 134.7, 129.4, 129.3, 128.2, 38.2; **AmdBr-C4Ph:** ^{13}C NMR (125 MHz, DMSO- d_6 , δ in ppm): 171.1, 141.3, 128.9, 128.8, 126.6, 34.9, 32.2, 28.4.

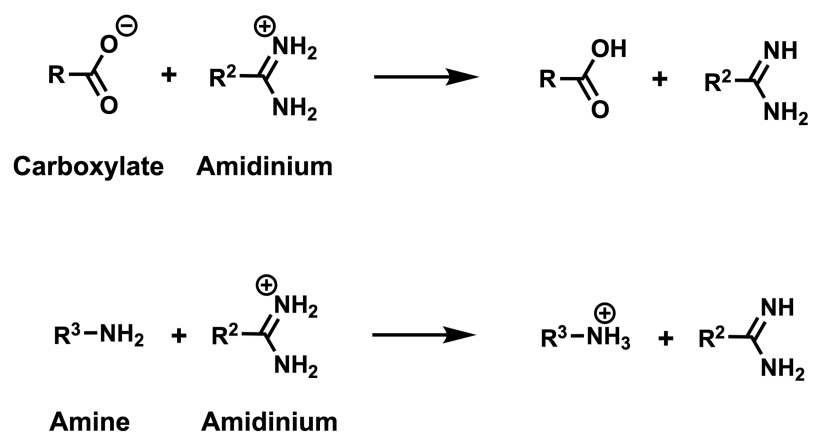
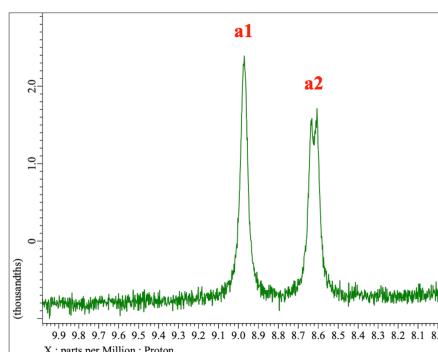
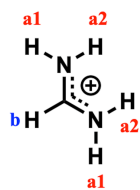
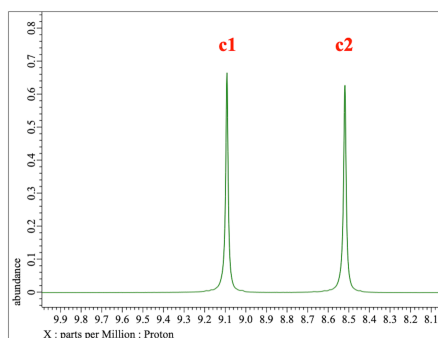
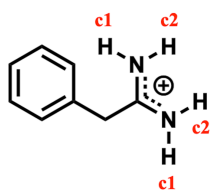


Fig. S3 Proton exchange reactions occur between ligands within a system.

FA



AmdBr-C2Ph



AmdBr-C4Ph

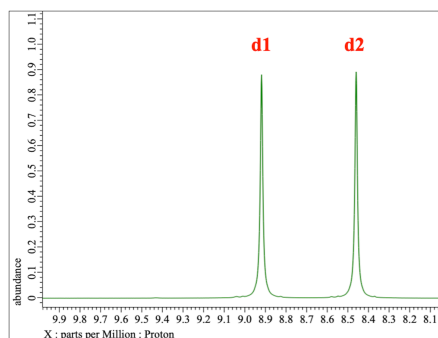
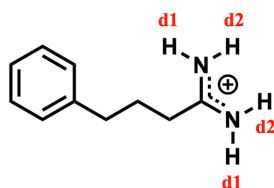
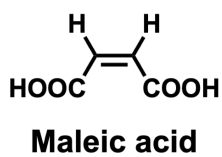


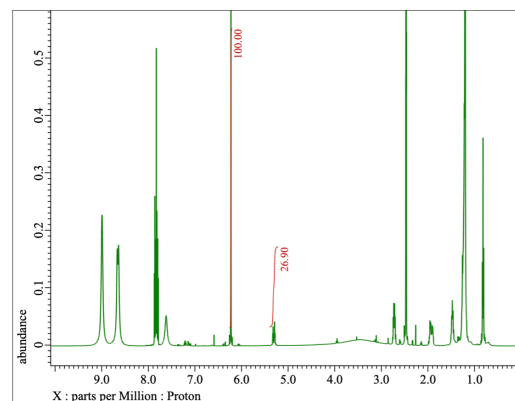
Fig. S4 ^1H NMR attribution of protons on nitrogen atoms of FA, AmdBr-C2Ph, and AmdBr-C4Ph.

At first glance, these protons, a1 and a2, c1 and c2, d1 and d2, seem to be equivalent based on the chemical structure, but they are not equivalent because they form a partial double bond between the nitrogens and carbon. In addition, the protons indicated as a2 is observed as a doublet due to coupling with proton b. Similarly, proton a1 should also be observed as a doublet; however, because it is in the cis position relative to proton b, the J-coupling value is smaller than that in the trans position, making it more likely to appear as a singlet. In contrast, in AmdBr-C2Ph and AmdBr-C4Ph, which do not have protons corresponding to b in FA, this coupling does not occur, therefore the protons on these nitrogens are observed as clear singlets.

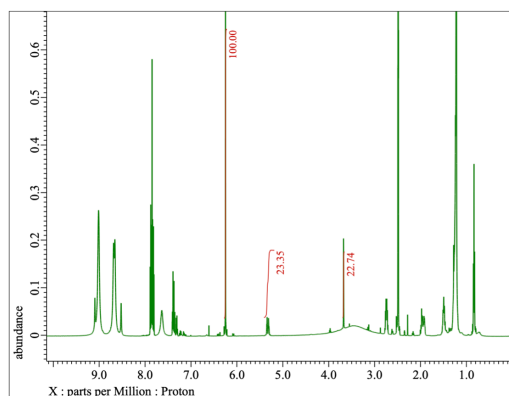
(a)



(b)



(c)



(d)

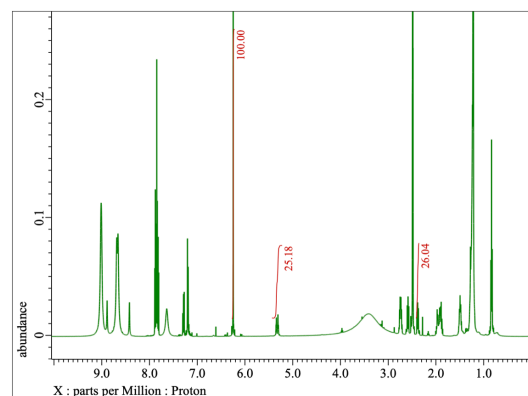


Fig. S5 (a) Molecular structure of maleic acid used as the reference material. In the ¹H NMR measurements, the proton on the carbon forming an *sp*² hybrid orbital showed a singlet peak around 6.3 ppm. (b), (c), and (d) show the ¹H NMR spectra of PeNCs with ligands of OAmBr, AmdBr-C₂Ph, and AmdBr-C₄Ph, respectively, which contain maleic acid.

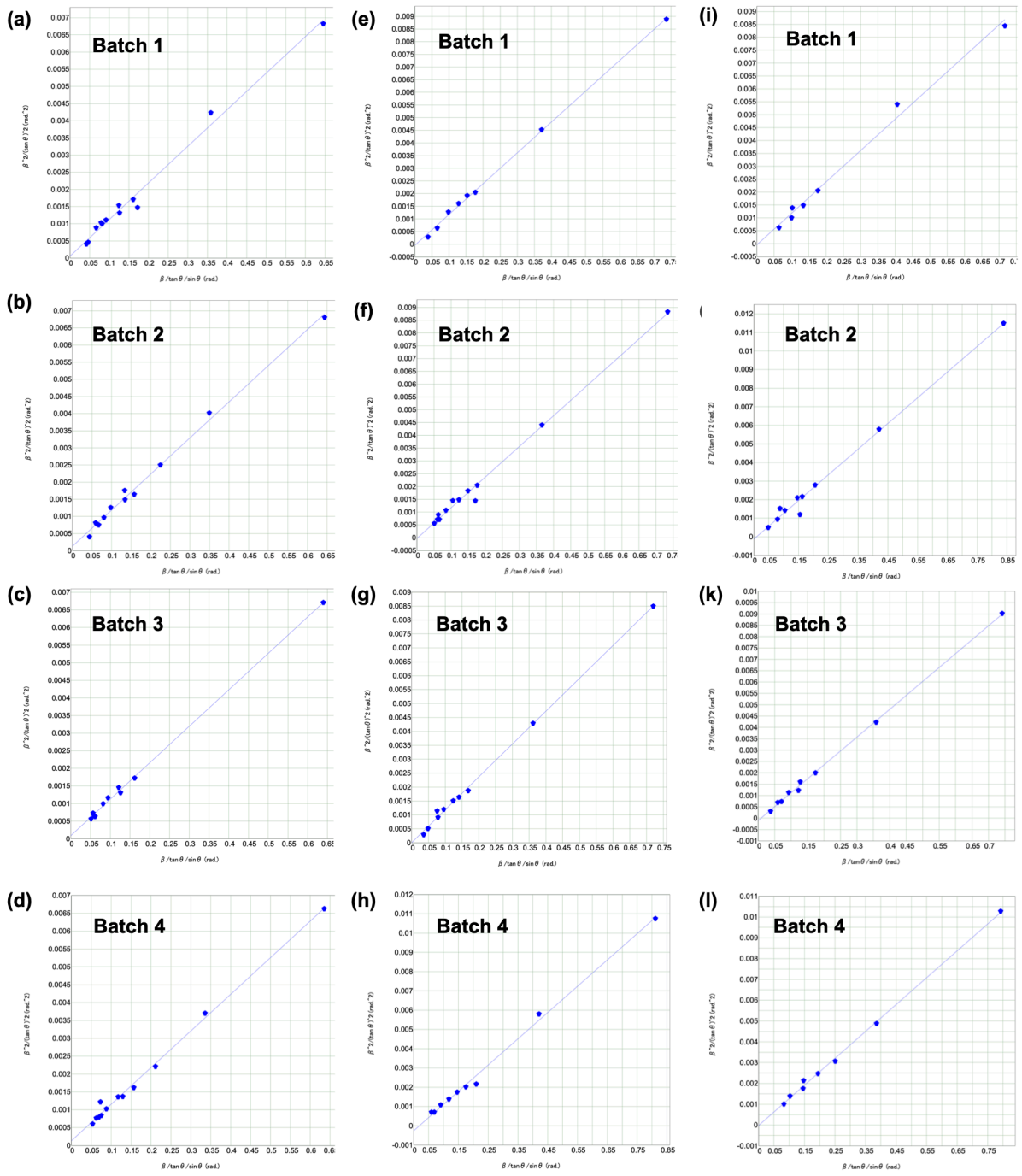


Fig. S6 The fitting plots based on the Halder-Wagner method for 4 batches of (a)-(d) OAmBr-PeNCs (e)-(h) AmdBr-C2Ph/PeNCs and (i)-(l) AmdBr-C4Ph/PeNCs.

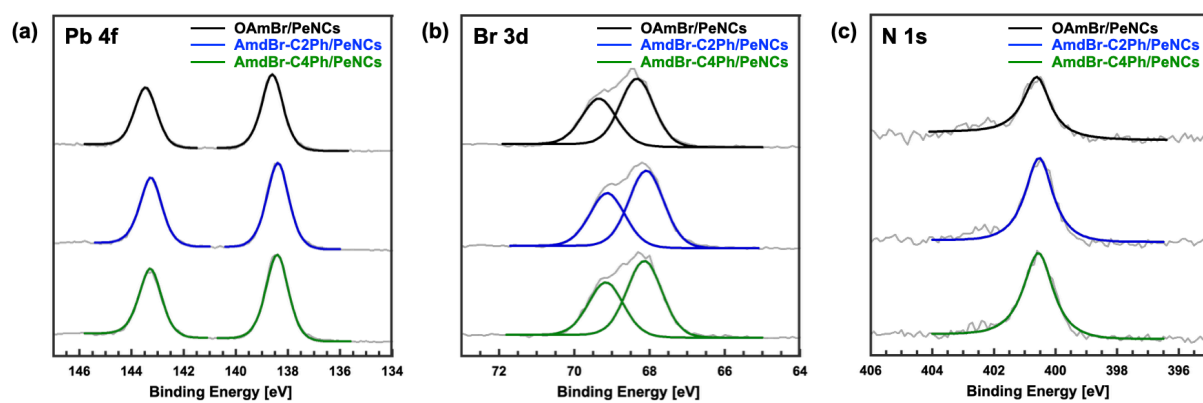


Fig. S7 XPS spectra of (a) Pb 4f, (b) Br 3d, and (c) N 1s.

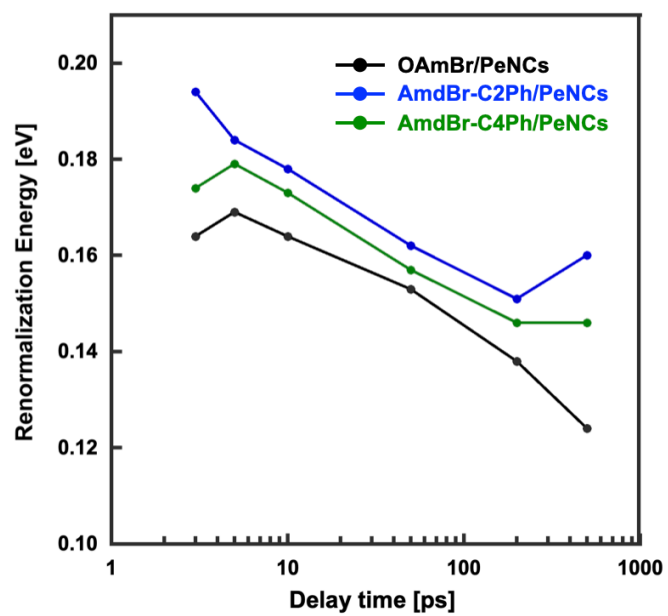


Fig. S8 The bandgap renormalization energy (ΔE_{rn}) at different delay times for PeNCs samples.

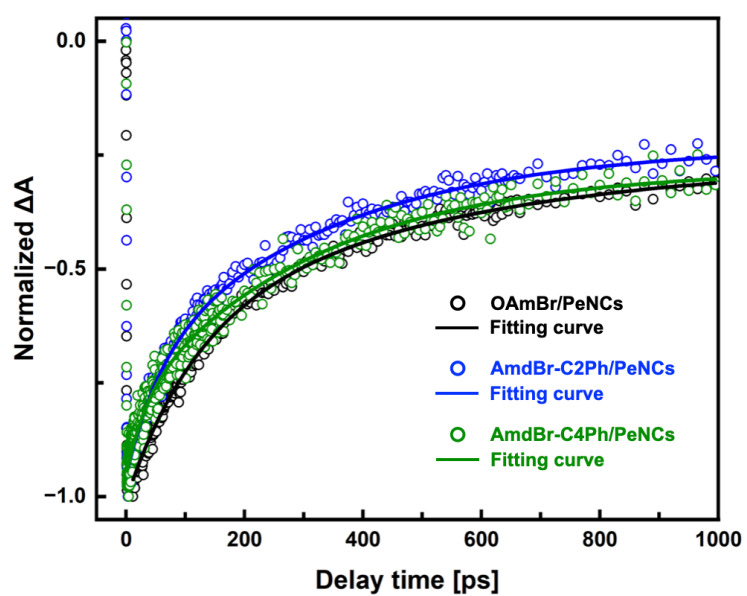


Fig. S9 The bleach recovery dynamics for the PeNCs samples at the photo bleaching peak.

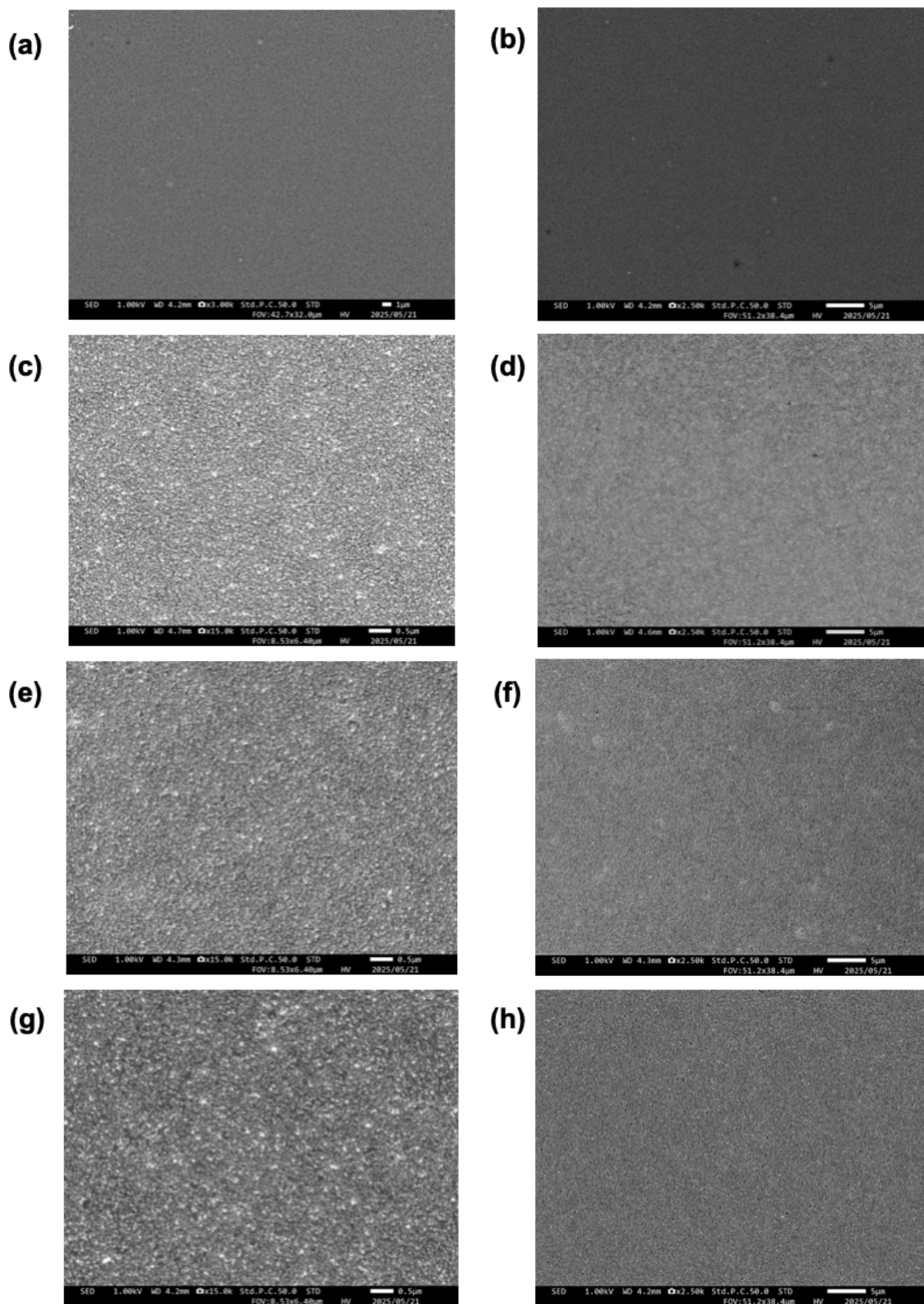


Fig. S10 SEM images of (a) and (b) PVK layer without PeNCs, (c) and (d) OAmBr/PeNCs, (e) and (f) AmdBr-C2Ph/PeNCs, (g) and (h) AmdBr-C4Ph/PeNCs. The left column shows high magnification (x 15.0k), and the right column shows low magnification (x 2.5k).

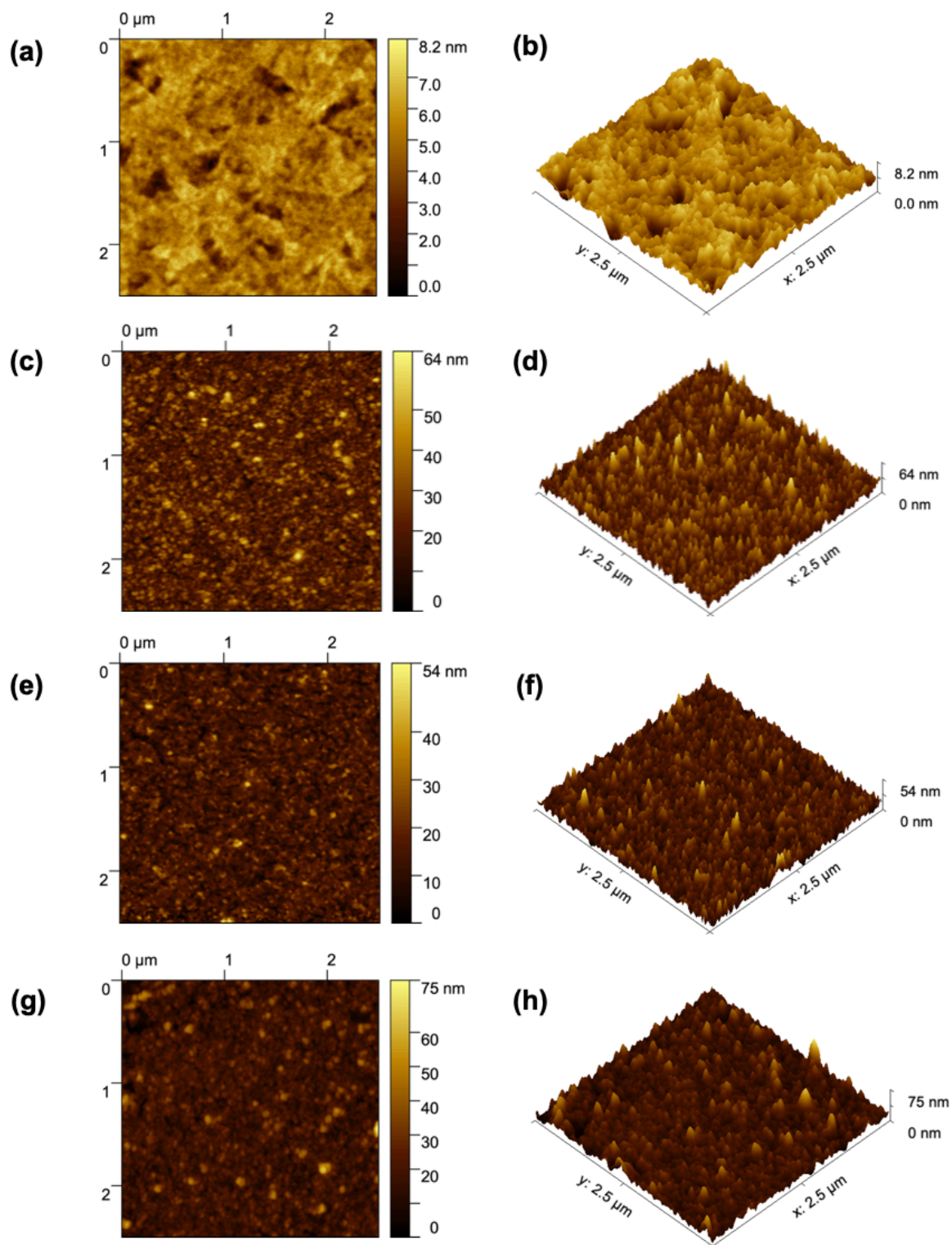


Fig. S11 Top view of AFM images of (a) PVK layer without PeNCs, (c) OAmBr/PeNCs, (e) AmdBr-C2Ph/PeNCs, (g) AmdBr-C4Ph/PeNCs and 3D view of AFM images of (b) PVK layer without PeNCs, (d) OAmBr/PeNCs, (f) AmdBr-C2Ph/PeNCs, (h) AmdBr-C4Ph/PeNCs.

Table S1 Crystal strain calculated from Halder-Wagner plots for four lots of each PeNCs.

	OAmBr/PeNCs	AmdBr-C2Ph/PeNCs	AmdBr-C4Ph/PeNCs
Batch 1	0.19	0	0
Batch 2	0.28	0	0
Batch 3	0.24	0	0
Batch 4	0.29	0	0
Avg.	0.25	0	0

Table S2 Summary of the emission wavelength (λ_{Em}), FWHM, and PLQY of each PeNCs sample.

Sample	λ_{Em} [nm]	FWMH [nm]	PLQY [%]
OAmBr/PeNCs	536	22.6	75
AmdBr-C2Ph/PeNCs	532	22.3	88
AmdBr-C4Ph/PeNCs	533	22.8	91

Table S3 The elemental ratios of Br/Pb and N/Pb measured by XPS

Sample	Br/Pb	N/Pb
OAmBr/PeNCs	3.06	0.754
AmdBr-C2Ph/PeNCs	3.43	0.864
AmdBr-C4Ph	3.30	0.910

Table S4 Quantification of surface ligands by ^1H NMR

Sample	PeNCs weight [mg]	OAmBr [μmol]	AmdBr-C2Ph [μmol]	AmdBr-C4Ph [μmol]	Total [μmol]
OAmBr/PeNCs	8.8	1.3	–	–	1.3
AmdBr-C2Ph/PeNCs	8.8	1.1	1.1	–	2.2
AmdBr-C4Ph/PeNCs	8.8	1.2	–	1.3	2.5

Table S5 The positions of photobleaching (PB) and photoinduced absorbance (PIA) peaks and calculated the bandgap renormalization energy (ΔE_m).

	Delay time [ps]	PB [nm]	PIA [nm]	ΔE_m
OAmBr/PeNCs	3	532	497	0.164
	5	532	496	0.169
	10	532	497	0.164
	50	534	501	0.153
	200	534	504	0.138
	500	534	507	0.124
AmdBr-C2Ph/PeNCs	3	526	486	0.194
	5	526	488	0.184
	10	526	489	0.178
	50	528	494	0.162
	200	529	497	0.151
	500	530	496	0.160
AmdBr-C4Ph/PeNCs	3	525	489	0.174
	5	525	488	0.179
	10	526	490	0.173
	50	527	494	0.157
	200	528	497	0.146
	500	529	498	0.146

Table S6 The fitted constants (A_1 and A_2), faster (τ_1) and slower (τ_2) times of the PeNCs samples for the fs-TA spectra.

Sample	τ_1 [ps]	A_1	τ_2 [ps]	A_2
OAmBr/PeNCs	114	0.36	487	0.39
AmdBr-C2Ph/PeNCs	56.0	0.23	341	0.49
AmdBr-C4Ph/PeNCs	33.3	0.15	317	0.52

Table S7 Summary of LED properties of PeNCs, turn-on voltage (V_{ON}), maximum luminance, current efficiency, and EQE.

Sample	$V_{ON}@1 \text{ cd/m}^2$ [V]	L_{MAX} [cd/m ²]	CE_{MAX} [cd/A]	EQE_{MAX} [%]
OAmBr/PeNCs	3.7	2,911	34.0	7.6
AmdBr-C2Ph/PeNCs	3.1	6,907	76.3	17.6
AmdBr-C4Ph/PeNCs	3.2	1,453	48.9	11.6

Table S8 Summary of RMS value of the PeNCs thin films.

Sample	RMS [nm]
PVK layer	0.967
OAmBr/PeNCs	7.316
AmdBr-C2Ph/PeNCs	5.013
AmdBr-C4Ph/PeNCs	6.410

Table S9 Summary of thickness of the PeNCs thin films.

Sample	Thickness [nm]
OAmBr/PeNCs	34.6 ± 1.15
AmdBr-C2Ph/PeNCs	34.4 ± 0.73
AmdBr-C4Ph/PeNCs	36.2 ± 0.94

Table S10 Previous studies of fabricated electroluminescent-type LEDs by designing and synthesizing ligands to prepare PeNCs.

Ref.	Color (Composition of PeNCs)	Ligands design	EQE _{MAX} before ligand exchange [%]	EQE _{MAX} after ligand exchange [%]	Improvement in EQE _{MAX} [%]
This work	Green (FAPbBr₃)	Aromatic ring & Short alkyl tail + Amidinium head + Bromide ion	7.6	17.6	10.0
²	Skyblue (CsPbBr ₂ Cl)	Zwitterionic head + Carbazole based tail	0.45*	0.73*	0.28
³	Green (CsPbBr ₃)	Conjugated linoleic acid	N/A	1.52	
³	Red (CsPbI ₃)	Conjugated linoleic acid	N/A	2.67	
⁴	Green (CsPbBr ₃)	Sulfobetaine-based zwitterionic ligands	N/A	~3.5	
⁵	Green (CsPbBr ₃)	Cross-linkable spacer ligands between QDs and hole transport layer	N/A	N/A	

* Read from the graph

Table S11 Previous studies in which the ligands were synthesized and introduced into PeNCs without the fabrication of an electroluminescent-type LEDs.

Ref.	Ligands
6	Zwitterionic ligands
7	Photo-crosslinkable zwitterionic ligand
8	Sulfonium bromide ligand
9	Ammonium salt polymer ligands
10	Polyzwitterion polymer ligand
11	Ligands with a benzoic acid framework

Table S12 Typical previous studies prepared PeNCs by ligand exchange and fabricated electroluminescent LED without ligand synthesis.

Ref.	Ligands	$E_{\text{EQE}}^{\text{MAX}}$ before ligand exchange [%]	$E_{\text{EQE}}^{\text{MAX}}$ after ligand exchange [%]	Improvement in $E_{\text{EQE}}^{\text{MAX}}$ [%]
¹²	2,2-diphenylethylamine	15.8	18.6	2.8
¹³	3-(decyldimethylammonio)propanesulfonate	5.1	12.17	7.07
¹⁴	Didodecyl dimethyl ammonium bromide (DDAB)	2.7	16.1	13.4
¹⁴	DDAB+OA	16.1	18.6	2.5
¹⁵	2-thiophenepropylamine bromide	3.2	10.5	7.3
¹⁶	2-Naphthalenesulfonic Acid	13.3	19.2	5.9
¹⁷	3-(N,N-dimethyloctadecylammonio)-propanesulfonate	0.6	1.4	0.8

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