Electronic supplementary information

Highly Efficient Room-temperature Phosphorescence and Afterglow Luminescence from Common Organic Fluorophores in 2D Hybrid Perovskites

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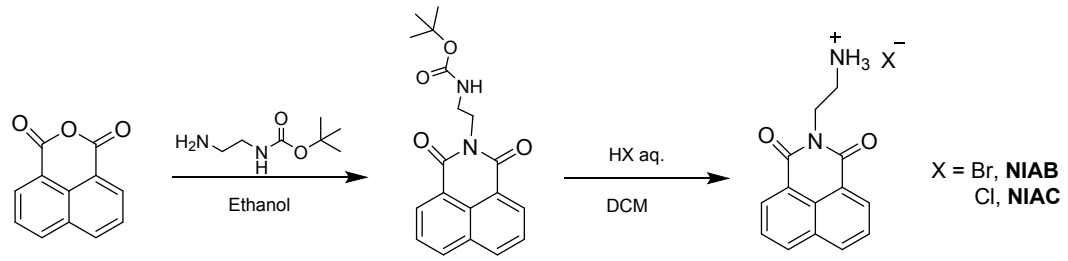


Scheme S1 Synthetic route of NIAB and NIAC.

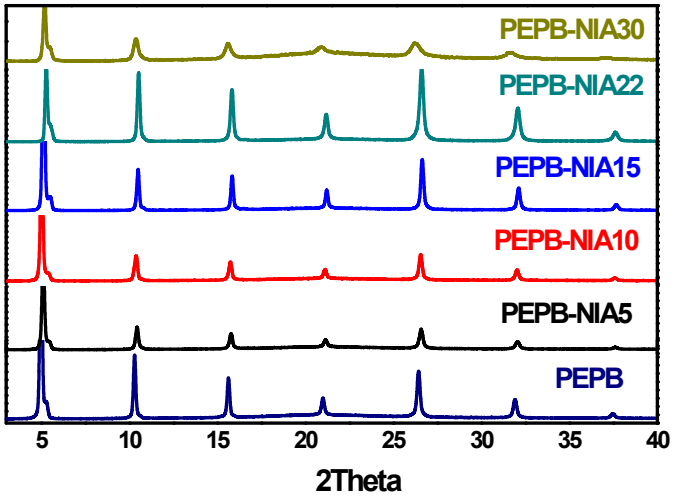


Fig. S1 XRD patterns for PEPB and PEPB-NIA.

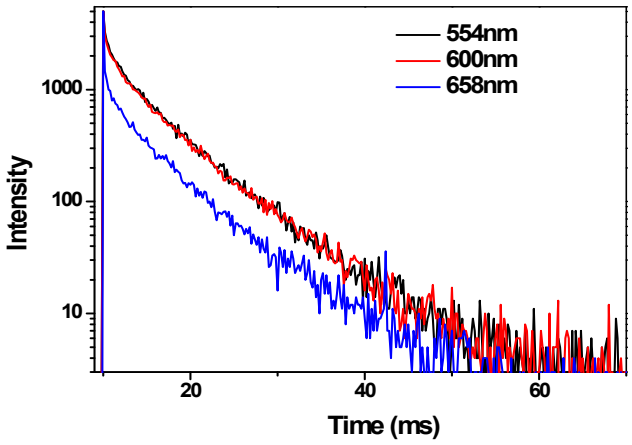


Fig. S2 Transient luminescence decays of PEPB-NIA5 film measured at different emission peaks.

Table S1 Lifetime data of PEPB-NIA5 and PEPB-NIA22 films.

Film	**λ, nm**	**τ_1, ms (%)**	**τ_2, ms (%)**	**τ_3, ms (%)**	**τ_{av}, ms**	**χ^2**
PEPB-NIA5	554	0.79 (6.34)	3.63 (32.48)	7.53 (61.18)	5.83	1.21
	600	0.79 (6.11)	3.60 (31.74)	7.64 (62.15)	5.94	1.06
	658	0.42 (6.51)	3.32 (36.01)	7.69 (57.48)	5.64	1.17
PEPB-NIA22	554	0.30 (4.24)	1.67 (25.36)	5.90 (70.40)	4.59	1.30
	601	0.73 (8.30)	2.95 (37.31)	7.08 (54.39)	5.01	1.19
	656	0.35 (6.80)	2.09 (30.65)	6.62 (62.55)	4.81	1.29

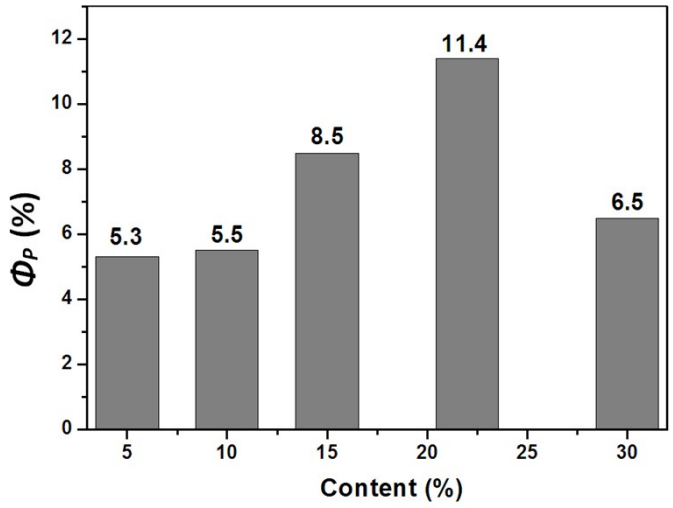


Fig. S3 Phosphorescent quantum yield (Φ_P) of the doping perovskite films (PEPB-NIA) with different content of NIAB.

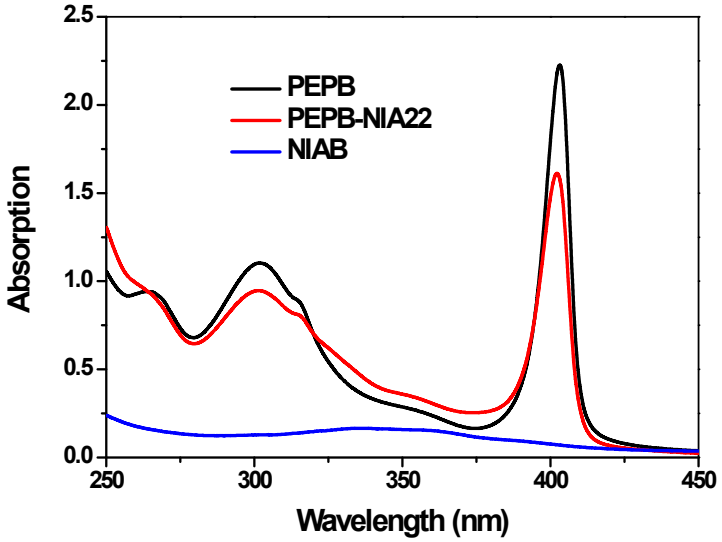


Fig. S4 Absorption spectra of PEPB, PEPB-NIA22, and NIAB in film.

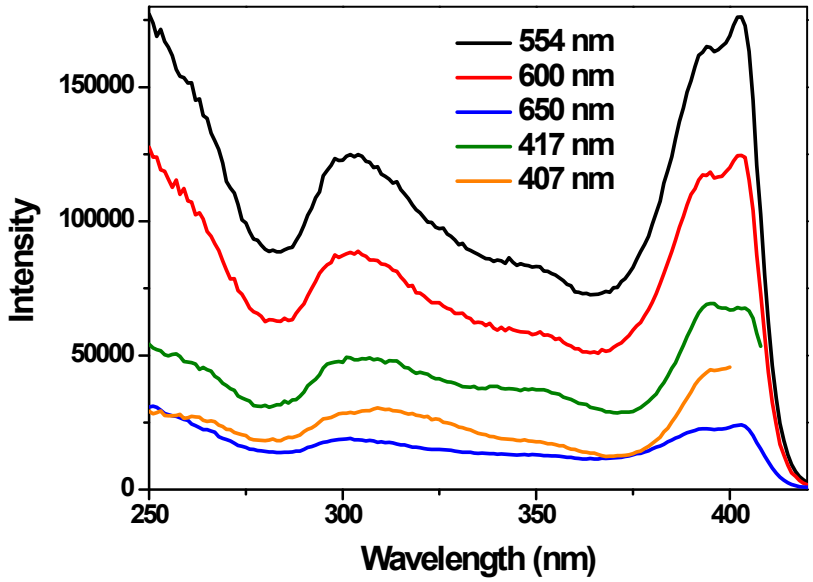


Fig. S5 Excitation spectra of PEPB-NIA22 film measured at different emission peaks.

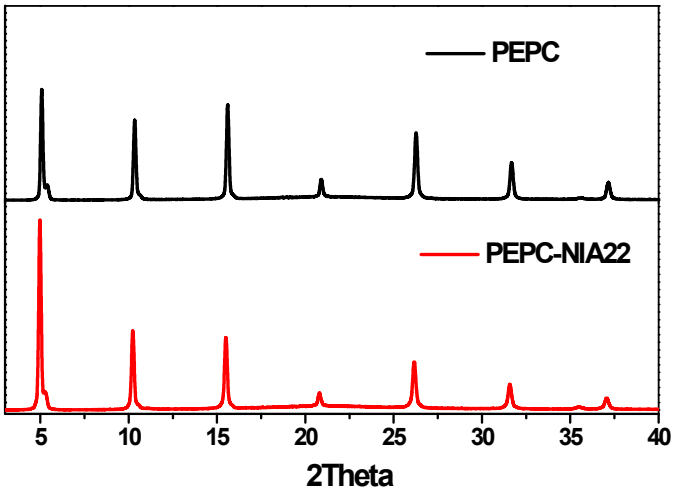


Fig. S6 XRD patterns for PEPC and PEPC-NIA22.

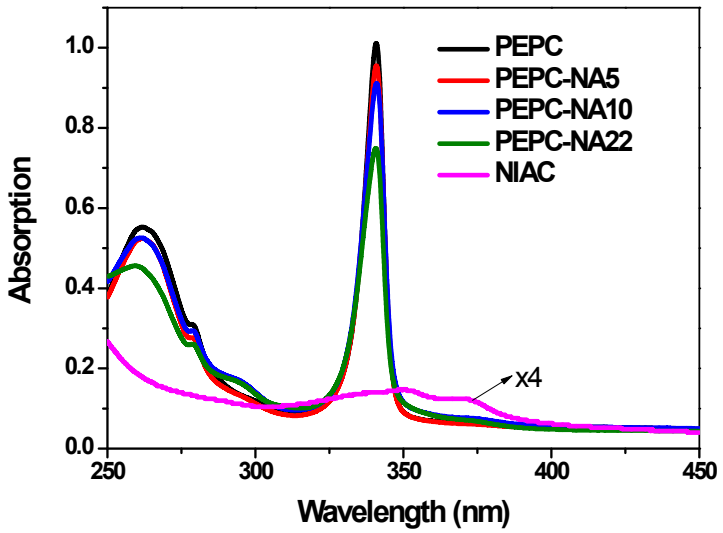


Fig. S7 Absorption spectra of PEPC, PEPC-NIAs, and NIAC in film.

Table S2 Lifetime data and phosphorescent quantum yield of PEPC-NIA22 film.

λ, nm	τ_1 (%)	τ_2 (%)	τ_{av}	χ^2	Φ_p, %
653	9.07 ms (7.74)	43.85 ms (92.26)	41.16 ms	1.232	4.21
596	4.47 ms (3.82)	42.20 ms (96.18)	40.76 ms	1.272	
550	15.30 ms (9.51)	44.80 ms (90.49)	41.99 ms	1.238	
500	5.88 ns (17.49)	15.03 ns (82.51)	13.43 ns	1.068	/

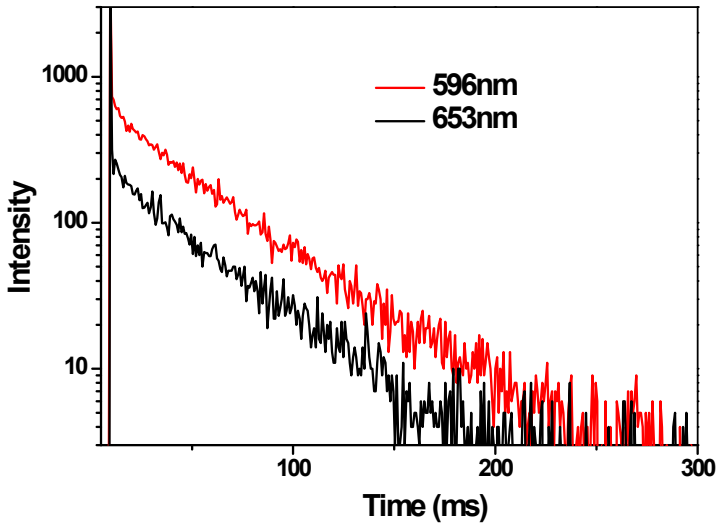


Fig. S8 Transient luminescence decays of PEPC-NIA22 film measured at different emission peaks.

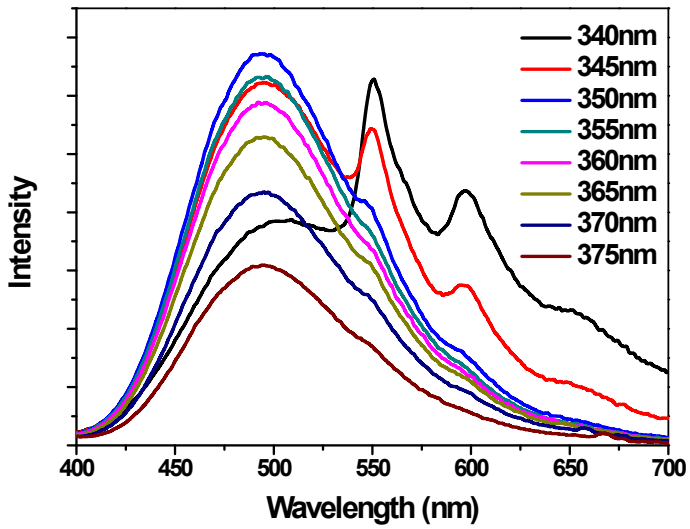


Fig. S9 Photoluminescent spectra of PEPC-NIA22 film excited by different wavelength.

Fig. S10 Photos of different luminescent states of the Chinese word of phosphorescence after 10 cycles of switching

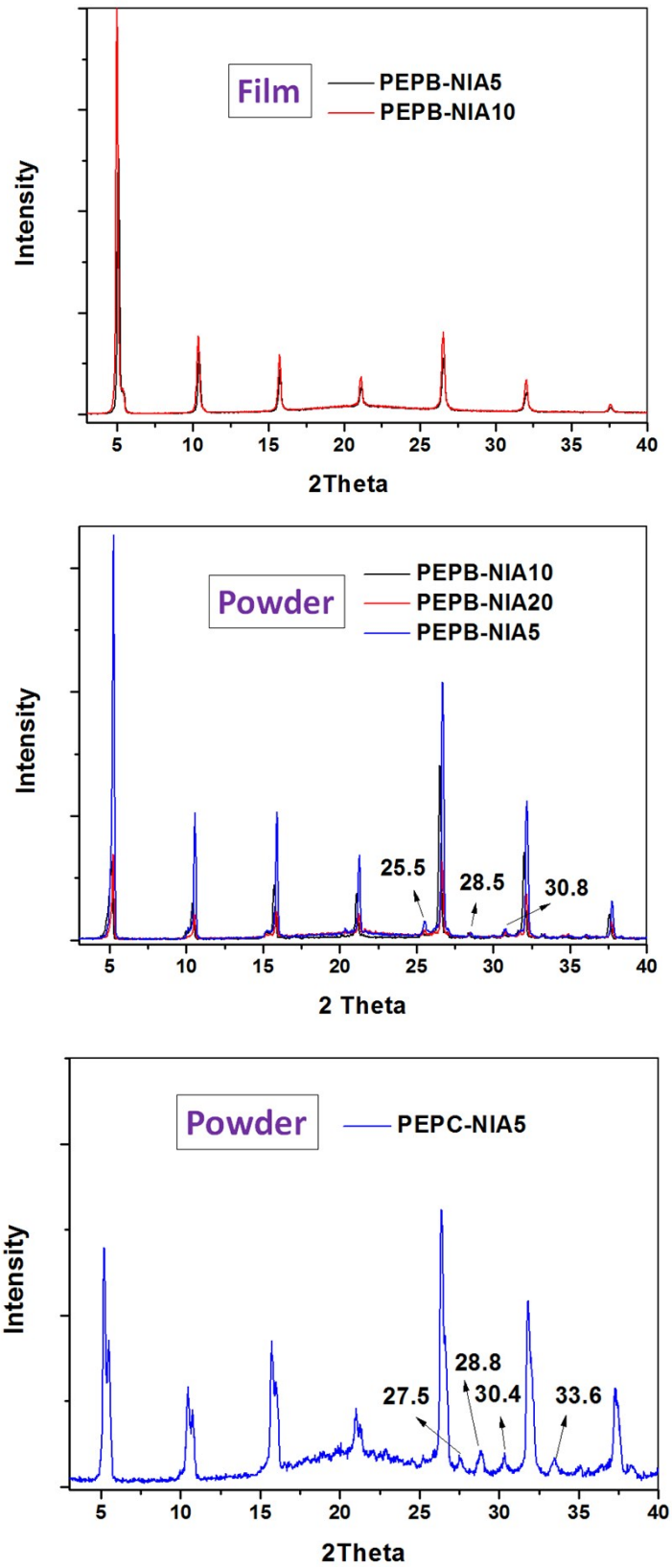


Fig. S11 XRD patterns of PEPB-NIAs and PEPC-NIA in powder, and PEPB-NIAs in film.

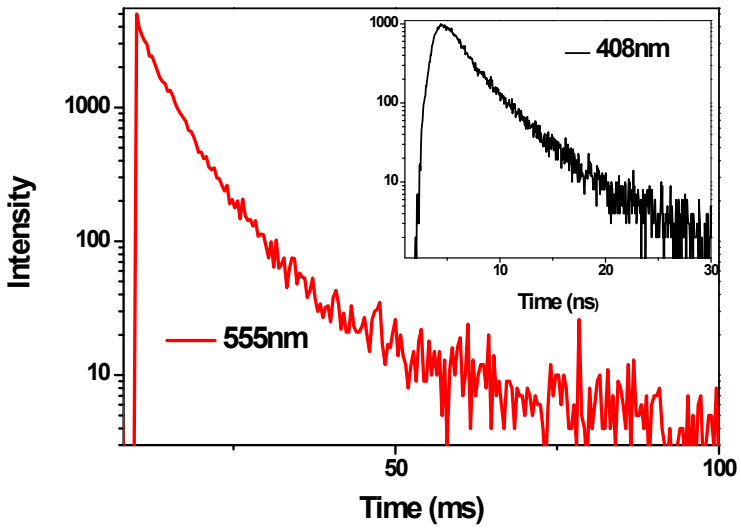


Fig. S12 Transient luminescence decays of PEPB-NIA5 powder measured at different emission peaks.

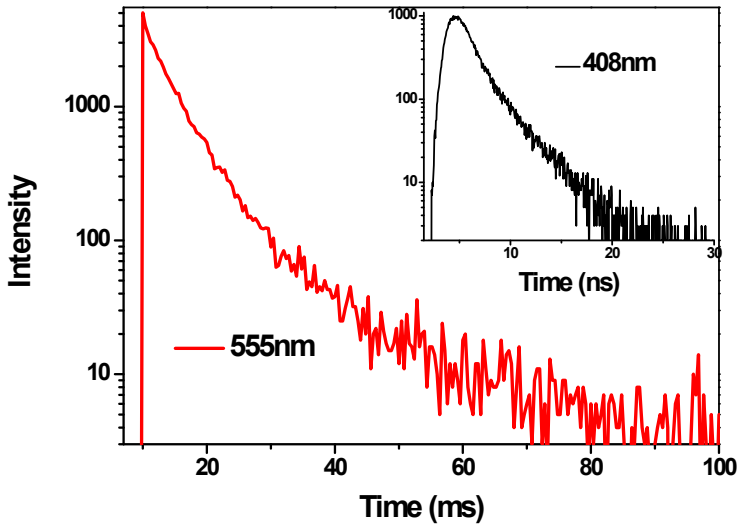


Fig. S13 Transient luminescence decays of PEPB-NIA10 powder measured at different emission peaks.

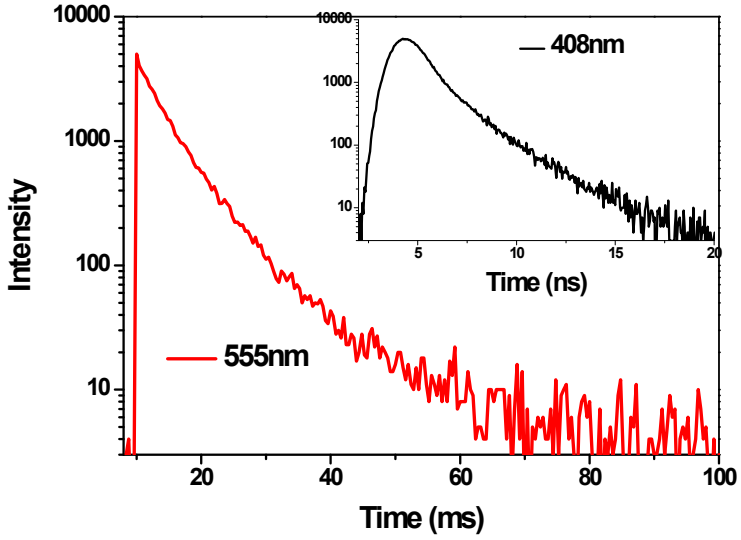


Fig. S14 Transient luminescence decays of PEPB-NIA20 powder measured at different emission peaks.

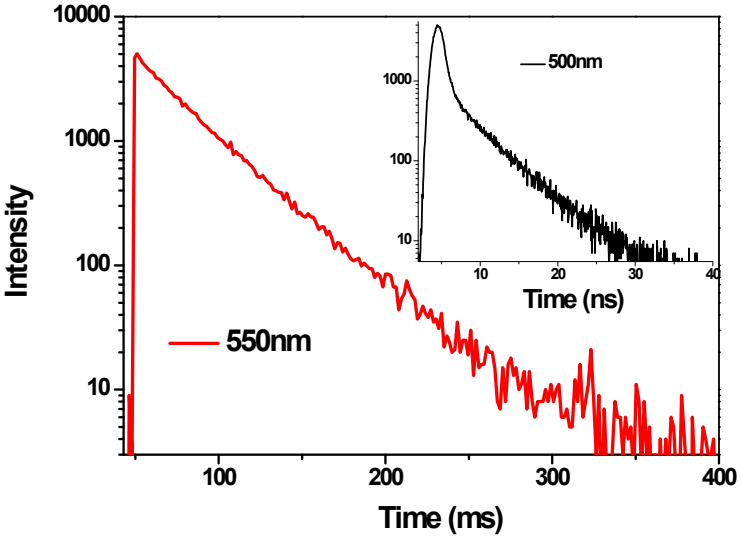


Fig. S15 Transient luminescence decays of PEPC-NIA5 powder measured at different emission peaks.

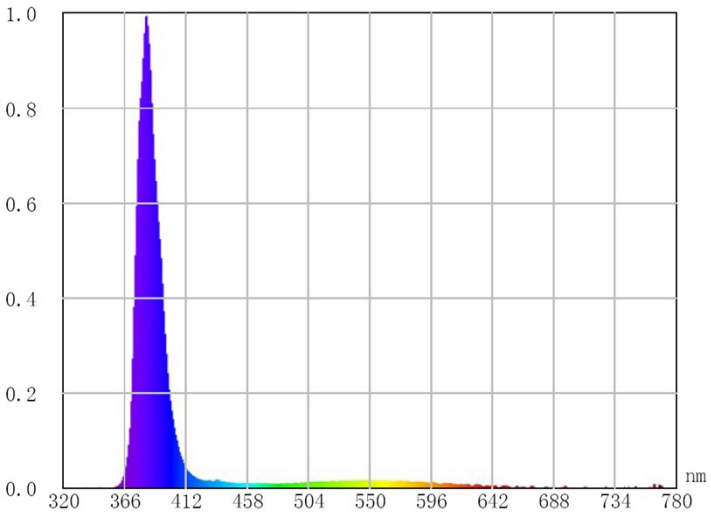


Fig. S16. Electroluminescent spectrum of UV-LED without perovskites.

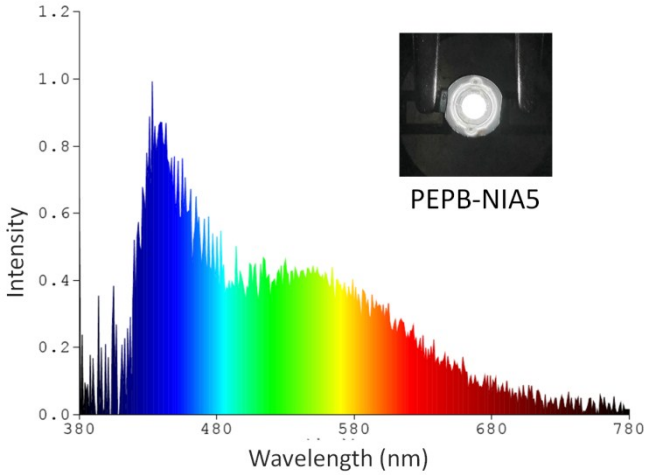


Fig. S17. Electroluminescent spectrum of UV-LED witht PEPB-NIA5.

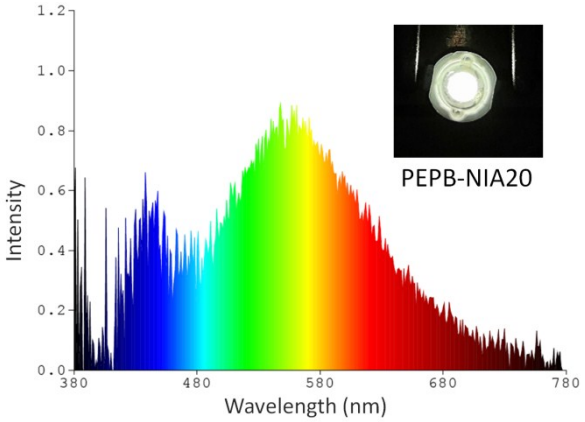
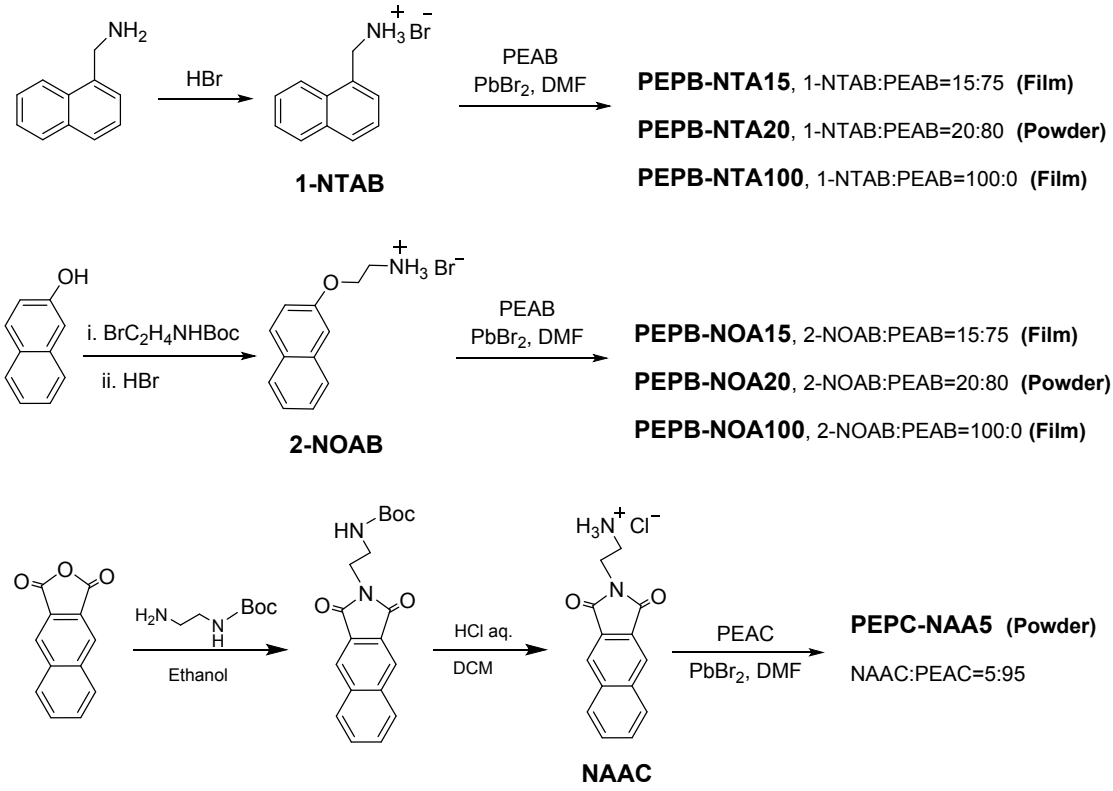


Fig. S18. Electroluminescent spectrum of UV-LED witht PEPB-NIA20.



Scheme S2 Synthetic route of 1-NTAB, 2-NOAB, NAAC, PEPB-NTA, PEPB-NOA and PEPC-NAA.

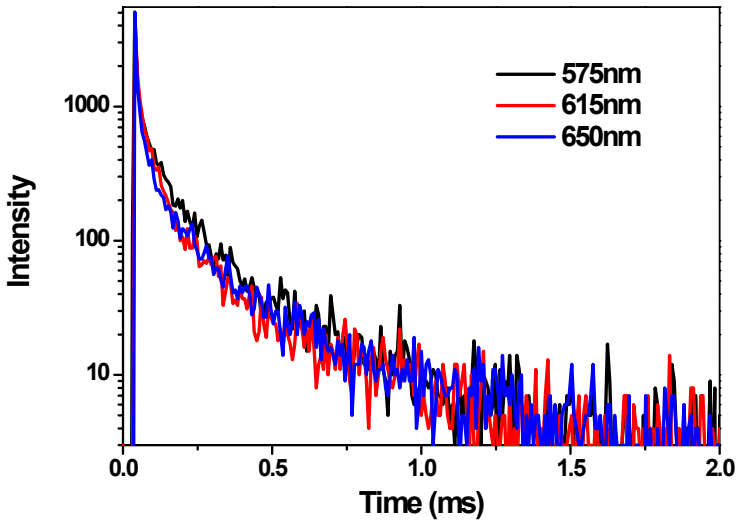


Fig. S19 Transient luminescence decays of PEPB-NTA100 film measured at different emission peaks.

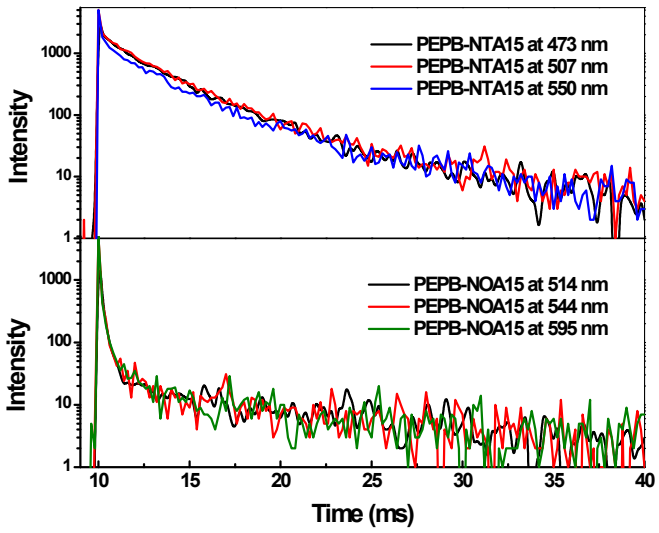


Fig. S20 Transient luminescence decays of PEPB-NTA15 and PEPB-NOA15 film measured at different emission peaks.

Table S3 Lifetime data and phosphorescent quantum yield of PEPB-NTA100, PEPB-NTA15 and PEPB-NOA15 films.

Film	**λ, nm**	**τ_1, ms (%)**	**τ_2, ms (%)**	**τ_3, ms (%)**	**τ_{av}, ms**	**χ^2**	**Φ_p, %**
PEPB-NTA100	575	0.014 (14.96)	0.087 (52.80)	0.394 (32.24)	0.175	1.318	0.41%
	615	0.029 (21.53)	0.160 (50.34)	0.979 (28.13)	0.362	1.344	
	650	0.038 (27.41)	0.252 (41)	1.10 (31.59)	0.462	1.235	
PEPB-NTA15	473	0.83 (12.72)	2.99 (76.29)	9.41 (10.99)	3.42	1.188	2.24
	507	0.59 (6.69)	2.69 (76.18)	8.55 (17.13)	3.56	1.239	
	550	0.32 (7.42)	2.50 (71.06)	8.36 (21.52)	3.60	1.152	
PEPB-NOA15	514	0.20 (52.57)	1.25 (9.70)	12.28 (37.73)	4.86	1.095	4.39
	544	0.21 (47.05)	0.98 (13.57)	11.33 (39.38)	4.47	1.112	
	595	0.21 (44.83)	1.66 (20.58)	16.46 (34.59)	6.13	1.167	

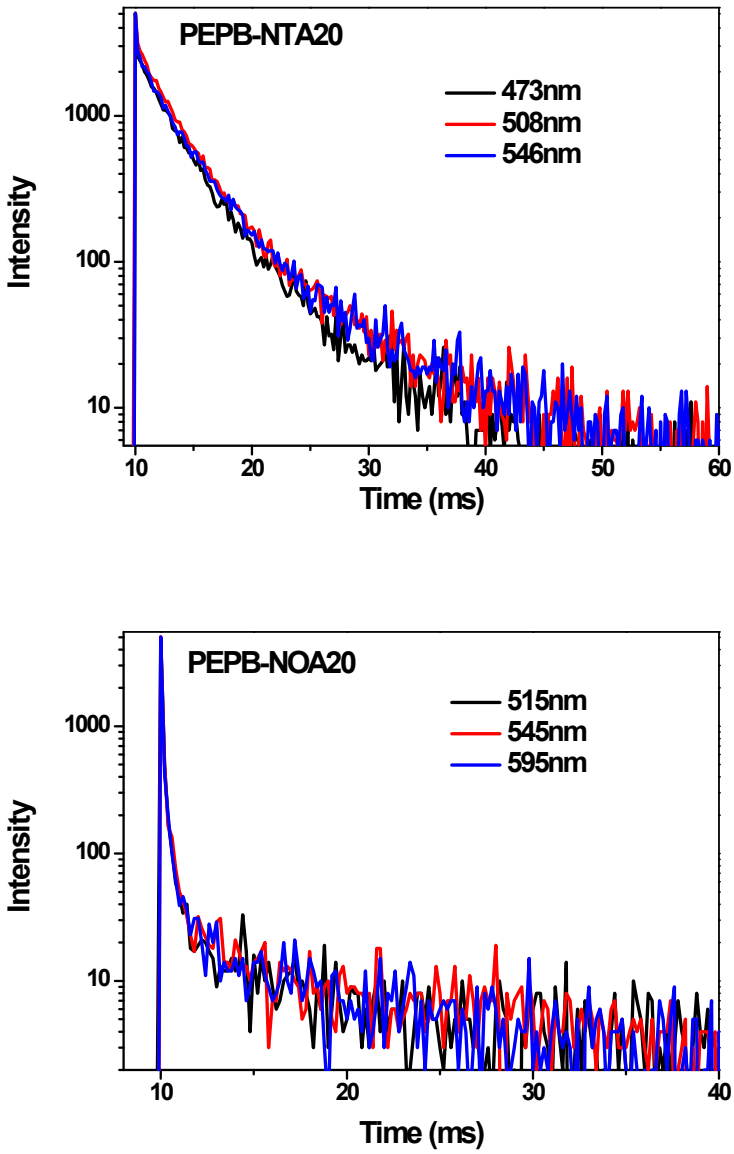


Fig. S21 Transient luminescence decays of PEPB-NTA20 and PEPB-NOA20 powders measured at different emission peaks.

Table S4 Lifetime data and phosphorescent quantum yield of PEPB-NTA20 and PEPB-NOA20 powders.

Powder	**λ, nm**	**τ_1, ms (%)**	**τ_2, ms (%)**	**τ_3, ms (%)**	**τ_{av}, ms**	**χ^2**	**Φ_p, %**
PEPB-NTA20	473	1.31 (8.50)	2.95 (72.68)	8.96 (18.82)	3.95	1.156	18.6
	508	0.52 (3.13)	2.92 (77.26)	10.52 (19.61)	4.34	1.323	
	546	1.23 (11.56)	3.35 (70.45)	11.77 (17.99)	4.62	1.415	
PEPB-NOA20	515	0.22 (50.57)	3.20 (17.40)	25.52 (32.03)	8.84	1.043	13.2
	545	0.19 (44.94)	1.29 (16.78)	14.74 (38.28)	5.94	1.277	
	595	0.23 (47.00)	2.24 (19.30)	18.79 (33.70)	6.87	1.220	

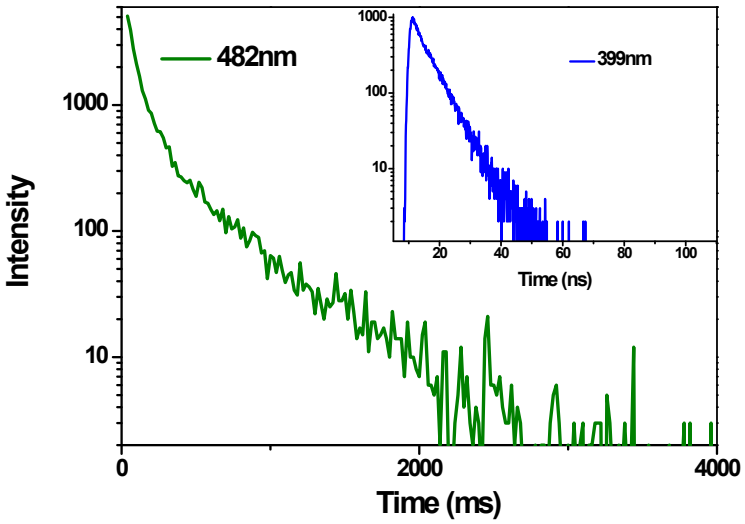


Fig. S22 Transient luminescence decays of PEPC-NAA5 powder measured at different emission peaks.

Table S5 Lifetime data and phosphorescent quantum yield of PEPC-NAA5 powder.

λ, nm	τ_1, (%)	τ_2, (%)	τ_3, (%)	τ_{av},	χ^2	Φ, %
399	1.06 ns (3.50)	5.49 ns (96.50)	/	5.33 ns	1.051	25.5%
482	31.21 ms (18.13)	103.13 ms (40.78)	457.59 ms (41.09)	235.74 ms	1.243	

Experimental section

Materials

Phenylethylammonium chloride (99.99%), phenylethylammonium bromide (99.99%), lead (II) bromide (99.99%) and lead (II) chloride (99.99%) were purchased from Xi'an polymer Light Technology Corp. 1,8-naphthalic anhydride (98%) was purchased from Shanghai Macklin Biochemical Corp. N-Boc-Ethylenediamine, 2-naphthol (98%), 1-naphthalenemethylamine, 2-(Boc-amino)ethyl bromide (98%), 2,3-naphthalenedicarboxylic anhydride (95%), HBr (48 wt.%, in water) were purchased from J&K Scientific LTD. HCl (36 wt.%, in water) was purchased from Sinopharm Chemistry Reagent Co. All reagents and solvents were used without further purification unless otherwise stated.

General methods

NMR spectra were measured in DMSO on a Bruker Ascend 400 FT-NMR spectrometer. ^{1}H NMR spectra were quoted relative to the internal standard tetramethylsilane. Absorption was obtained on a Shimadzu UV-2600 spectrophotometer. The crystalline structure of samples was confirmed by Powder X-ray diffraction (PXRD) using a Rigaku Dmax 2500 diffractometer with Cu-$K\alpha$ radiation (λ= 1.54056 Å) with a step size of 5°/min. Steady-state photoluminescence spectra and quantum yield of the samples were obtained at the room temperature using a Edinburgh FS5 spectrofluorometer with an integrating sphere for absolute photoluminescence quantum yield determination. Time-resolved photoluminescence decay curves were obtained using a FLS920 Fluorescence Spectrometer.

Synthesis of NIAB, NIAC and NAAC salt:

N-Boc-Ethylenediamine (1.60g, 10mmol) was mixed with Naphthalic anhydride (1.98g, 10mmol) in 50 ml of ethanol, and heated to reflux for 2h. The mixture was cooled and recrystallized in ethanol to give N-(2-ethyl-NH-Boc)-naphthalimide after filtered, and dried in the vacuum oven at 80 °C for 24h.

Then, N-(2-ethyl-NH-Boc)-naphthalimide (340 mg, 1mmol) in dichloromethane was reacted with 0.8 ml of HX (X=Cl, Br) aqueous solution (4M) at room temperature for 4h. During the process of reaction, more and more powder deposits were

precipitated out. The powders were filtered, washed with acetone, and dried in the vacuum oven at 60 °C for 24 h to give the corresponding white ammonium salt in a high yield of more than 90%.

NIAB. HBr aqueous solution was used. ^{1}H NMR (400 MHz, DMSO): δ 8.52(t, J=5.6 Hz and 8 Hz, 4H), 7.91 (t, J=8 Hz and 7.6 Hz, 2H), 7.82 (s, 3H), 4.32 (t, J=6 Hz and 5.6 Hz, 2H), 3.12 (t, J=5.6 Hz, 2H)

NIAC. HCl aqueous solution was used. ^{1}H NMR (400 MHz, DMSO): δ 8.51 (t, J=7.6 Hz and 9.6 Hz, 4H), 8.01 (s, 3H), 7.90 (t, J=8 Hz, 2H), 4.33 (t, J=6 Hz, 2H), 3.15 (t, J=6 Hz, 2H).

NAAC. HCl aqueous solution was used. ^{1}H NMR (400 MHz, DMSO): δ 8.55 (s, 2H), 8.28 (dd, J=3.6 Hz and 3.2 Hz, 2H), 8.19 (s, 3H), 7.79 (dd, J=3.2 Hz, 2H), 3.92 (t, J=6 Hz, 2H), 3.13 (t, J=6 Hz, 2H).

Synthesis of 1-NTAB salt

An aqueous HBr solution (0.5 ml, 4 M) was reacted with 1-naphthalenemethylamine (157 mg, 1 mmol) in dichloromethane under stirring at ambient temperature for 2h. The corresponding ammonium bromide was obtained in the yield of 93%. ^{1}H NMR (400 M Hz, DMSO): δ 8.31 (s, 3H), 8.16 (d, J=8.8 Hz, 1H), 8.01 (t, J=8.8 Hz and 8 Hz, 2H), 7.63 (m, 4H), 3.56 (s, 2H).

Synthesis of 2-NOAB salt

First, to a mixture of 2-Naphthol (360 mg, 2.5 mmol), NaH (60% dispersion in mineral oil, 120 mg, 3 mmol), and DMF (10 mL) was added 2-(Boc-amino)ethyl bromide (672 mg, 3 mmol). The mixture was stirred at room temperature for 12 h and then extracted with EtOAc. The combined organic extracts were washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give crude product. Then, the product was purified by recrystallization in ethanol.

2-NOAB salt was prepared as the synthetic method of NIAB described above in a yield of 90%. ^{1}H NMR (400 MHz, DMSO): δ 8.07 (s, 3H), 7.86 (dd, J=8.8 Hz and 6.8 Hz, 3H), 7.49 (t,J=7.6 Hz and 7.2 Hz, 1H), 7.40 (m, 2H), 7.22 (dd, J=2.8 Hz and 2.4 Hz, 1H), 4.31 (t, J=5.2 Hz and 4.8 Hz ,2H), 3.31 (t, J=7.3 Hz and 4.8 Hz, 2H).

Synthesis of PEPB-NIA films

Phenylethylammonium bromide (PEAB) was mixed with NIAB salt, lead bromide ($PbBr_2$) and dissolved in 0.25 mL of dimethylformamide (DMF). The solution was dispersed on a quartz substrate by spin-coating at 3000 rpm for 30 s, and annealed at 100 °C under nitrogen in an oven. The used amount of three kinds of bromides is listed in Table S6.

Synthesis of PEPC-NIA films

Phenylethylammoniumchloride (PEAC) was mixed with NIAC salt, lead chloride ($PbCl_2$), and dissolved in 0.25 mL of dimethylsulfoxide (DMSO). The solution was dispersed on a quartz substrate by spin-coating at 4000 rpm for 30 s, and annealed at 100 °C under nitrogen in an oven. The used amount of three kinds of chlorides is listed in Table S7.

Synthesis of PEPB-NIA powders

To the precursor solutions synthesized PEPB-NIA films was added 4 mL of acetone and vigorously stirred at room temperature for 30 min until most of the white powders were formed. The powders were filtered through a paper, washed with acetone, and dried in a vacuum oven at 80 °C for 24 h.

Synthesis of PEPC-NIA powder

To the precursor solutions synthesized PEPC-NIA film was slowly added 2 mL of acetone and vigorously stirred at room temperature for 30min until most of the white powders were formed. The powders were filtered through a paper, washed with acetone, and dried in a vacuum oven at 80 °C for 24 h.

PEPB-NTA, PEPB-NOA, and PEPC-NAA films and powders were preparation as described above.

Production of Encryption ink

49.1mg of phenylethylammoniumchloride (PEAC) and 24.3mg of NIAC was mixed with 55.6mg of lead chloride ($PbCl_2$) and dissolved in 1 mL of dimethylsulfoxide (DMSO). The solution was stirred at 70 °C for 3h.

LED devices

Light-emitting diodes (LEDs) used for the white electroluminescence were supplied by Shenzhen Looking Long Technology Co. The perovskite powders were firstly mixed with stoichiometric pouring sealant (HN3153-TCA/B), and then stirred for 15 min. After deaeration in vacuum oven at room temperature, the mixture was droped on top of the LED chip. They consist of a fully packaged Epileds InGaN LED Chips with an emission wavelength of about 380 nm. The forward current of the LEDs is 350 mA. Electroluminescence (EL) measurements of the LEDs were carried out at room temperature using an Everfine HAAS-2000. For the light collection the LEDs were placed inside a 30 cm diameter integrating sphere coupled to a High Accuracy Array Spectroradiometer (wavelength accuracy <0.3nm) and a programmable test power LED300E.

Table S6. Feeding amount of three kinds of bromides used in synthesis of PEPB-NIA.

	PEAB, mg (mmol)	NIAB, mg (mmol)	$PbBr_2$, mg (mmol)
PEPB	20.2 (0.1)		18.35 (0.05)
PEPB-NIA5	19.19 (0.095)	1.61 (0.005)	18.35 (0.05)
PEPB-NIA10	18.18 (0.09)	3.21 (0.01)	18.35 (0.05)
PEPB-NIA15	17.17 (0.085)	4.82 (0.015)	18.35 (0.05)
PEPB-NIA22	15.76 (0.078)	7.06 (0.022)	18.35 (0.05)
PEPB-NIA30	14.14 (0.07)	9.63 (0.03)	18.35 (0.05)

Table S7. Feeding amount of three kinds of chlorides used in synthesis of PEPC-NIA.

	PEAC, mg (mmol)	NIAC, mg (mmol)	$PbCl_2$, mg (mmol)
PEPC	15.75 (0.1)		13.9 (0.05)
PEPC-NIA5	14.96 (0.095)	1.38 (0.005)	13.9 (0.05)
PEPC-NIA10	14.18 (0.09)	2.77 (0.01)	13.9 (0.05)
PEPC-NIA22	12.29 (0.078)	6.08 (0.022)	13.9 (0.05)