

**Electronic Supplementary Information**

# Enhanced Nonlinear Optical Performance of Perovskite Films Passivated by Porphyrin Derivatives

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## Experimental Procedures

**1. Synthesis of methylammonium iodide (MAI).** HI aqueous solution was purified by using tributyl phosphate in chloroform with the concentration of 0.36 M three times until the colorless solution layer was separated and obtained. The HI was added dropwise to the  $\text{CH}_3\text{NH}_2$  (10 mL, 20 mmol) in tetrahydrofuran (THF, 30 mL), the mixture solution was stirred for 4 h at 0 °C under  $\text{N}_2$  atmosphere. After the reaction was completed, the solvent was removed and the white solid was washed many times with diethyl ether ( $\text{Et}_2\text{O}$ ,  $3 \times 100$  mL) to afford MAI in 70% yield.

**2. Preparation of 5,10,15,20-tetraphenylporphyrin.** A mixture of pyrrole (1.34 g, 0.02 mmol) and benzaldehyde (2.12 g, 0.02 mmol) in propionic acid (120 mL) was refluxed for 4 h under air atmosphere. After the reaction, the solution was cooled to 0 °C overnight, filtrated and washed with MeOH many times to give the purple powder product (0.79 g, 16%).  $^1\text{H}$  NMR (400 MHz,  $\text{CHCl}_3$ -*d*, TMS,  $\delta$ /ppm): 8.86 (m, 8H), 8.21 (m, 6H), 8.13 (m, 2H), 7.75 (m, 10H), -2.77 (s, 2H).

**3. Preparation of 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (1).** To a solution of 5,10,15,20-tetraphenylporphyrin (0.4 g, 0.65 mol) in dichloromethane (DCM) (60 mL) with 65 wt% concentrated  $\text{HNO}_3$  (3.5 mL, 0.05 mol) was added dropwise slowly at 0 °C. The mixture was stirred for 2 h and then slowly neutralized with diluted ammonium solution. The organic layer was extracted with DCM ( $2 \times 100$  mL) and separated. The water layer was extracted with DCM many times. The combined organic extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel, DCM : PE = 1 : 1) and recrystallized from MeOH/DCM to give 1 as a red powder (0.24 g, 57%).  $^1\text{H}$  NMR (400 MHz,  $\text{CHCl}_3$ -*d*, TMS,  $\delta$ /ppm): 8.86(m, 6H), 8.71(m, 2H), 8.55(d,  $J = 12$  Hz, 2H), 8.32(d,  $J = 12$  Hz, 2H), 8.13 (m, 6H), 7.75 (m, 9H), -2.74 (s, 2H).

**4. Preparation of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (2).** 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (100 mg, 0.15 mmol) was dissolved in concentrated HCl (40 mL), then SnCl<sub>2</sub>·2H<sub>2</sub>O (1.5 g, 0.007 mol) was dissolved in concentrated HCl (10 mL) was added carefully. The reaction solution was heated and stirred at 70 °C for 7 h. After the reaction, the mixture was quenched with ice water and slowly neutralized with diluted ammonium solution to PH = 7. The organic layer was extracted with DCM and separated. The water layer was extracted with DCM many times. The combined organic extracts were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The residue was purified by column chromatography (silica gel, DCM : PE = 1 : 1) to give 2 as a purple powder (64 mg, 68%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>-d, TMS, δ/ppm): 8.86(m, 6H), 8.71(m, 2H), 8.21(m, 6H), 8.13 (d, *J* = 4 Hz, 2H), 7.75 (m, 9H), 4.02 (s, 2H), -2.74 (s, 2H).

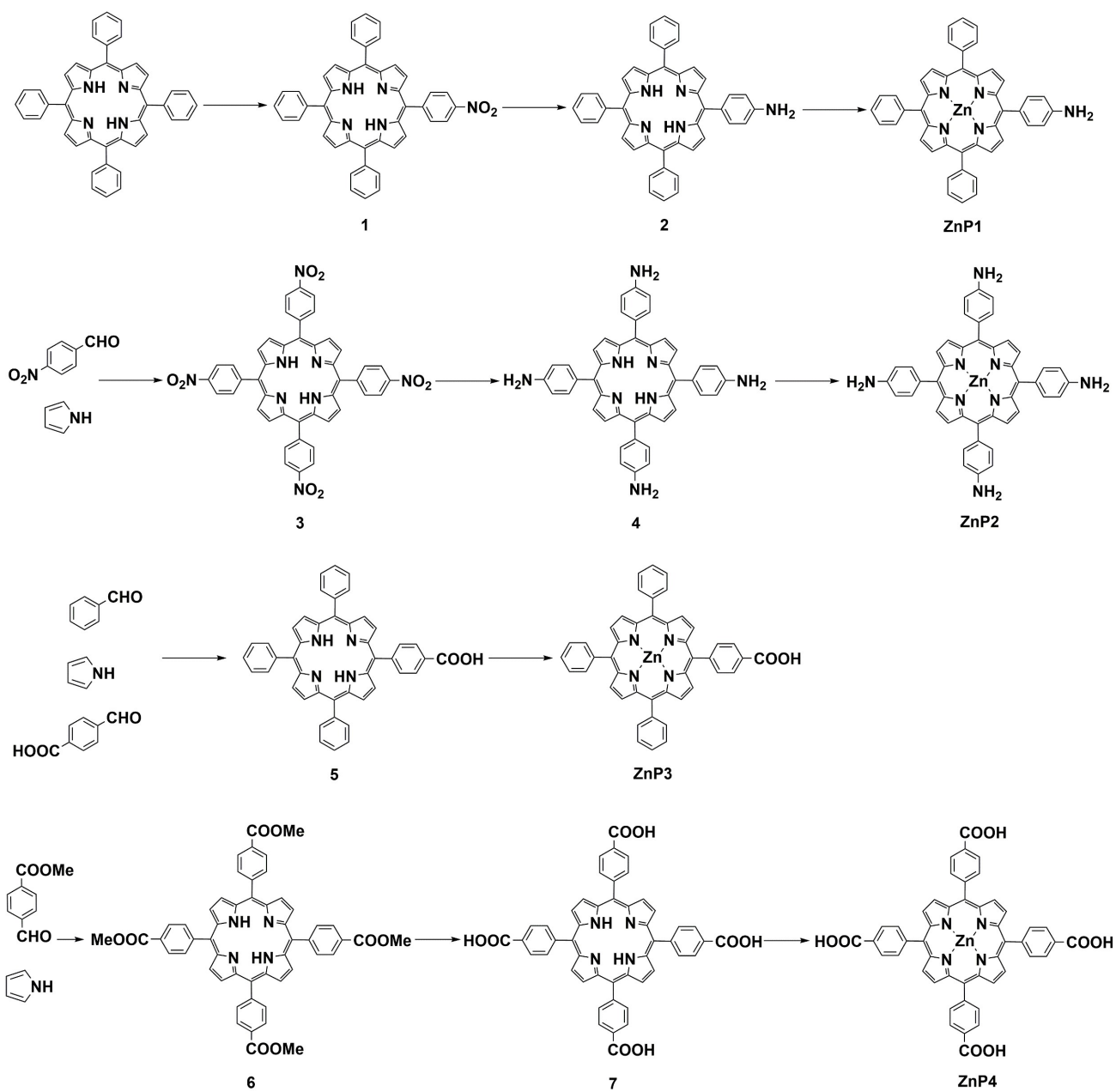
**5. Preparation of 5,10,15,20-tetrakis(4-nitrophenyl)porphyrin (3).** A mixture of *p*-nitrobenzaldehyde (3.7 g, 24.48 mmol) and acetic anhydride (4 mL, 42 mmol) in propionic acid (100 mL) was refluxed under air atmosphere, then pyrrole (1.68 mL, 24 mmol) dissolved in propionic acid (3.3 mL) was added dropwise and the mixture was refluxed for 1 h. After the reaction, the solution was cooled to 0 °C and let it stand overnight, filtrated and washed with MeOH many times to give 3 as a purple powder product (1.4 g, 28%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>-d, TMS, δ/ppm): 8.24 (s, 8H), 7.75 (d, *J* = 8.14 Hz, 8H), 7.65 (d, *J* = 8.14 Hz, 8H), -2.69 (s, 2H).

**6. Preparation of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (4).** Following the synthesis procedure for 2, the reaction mixture of 3 (1 g, 1.25 mmol), SnCl<sub>2</sub>·2H<sub>2</sub>O (4.5 g, 20 mmol) in concentrated HCl (70 mL) afforded 4 as a purple powder (0.45 g, 53%). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, TMS, δ/ppm): 8.88 (s, 8H), 7.92–7.76 (m, 8H), 7.07–6.92 (m, 8H), 5.58 (s, 8H), -2.75 (s, 2H).

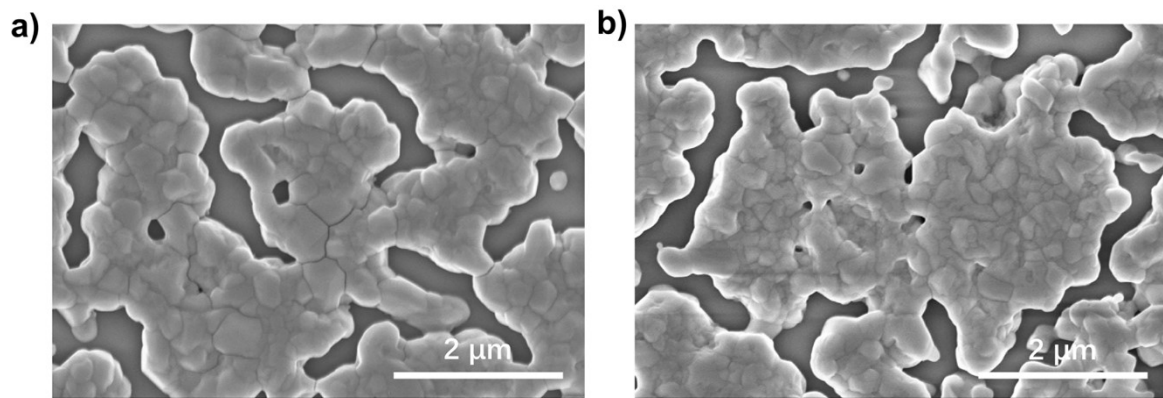
**7. Preparation of 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (5).** A mixture of 4-formylbenzoic acid (2.62 g, 17.5 mmol) and benzaldehyde (5.56 g, 52.4 mmol) in propionic acid (220 mL) was heated to 150 °C until aldehyde compounds were dissolved completely. Then pyrrole (4.8 mL, 70 mmol) in propionic acid (30 mL) was added dropwise and the mixture was refluxed for 1 h. After the reaction, the solution was cooled to room temperature. Removing the solvent and the residue was dissolved in ethyl acetate (EA). The organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel, EA : PE = 1 : 1) to give 5 as a purple powder (2.08 g, 18%). <sup>1</sup>H NMR (600 MHz, CHCl<sub>3</sub>-*d*, TMS, δ/ppm): 9.02–8.71 (m, 4H), 8.56–8.47 (m, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.29–8.08 (m, 3H), 7.77 (dddd, *J* = 14.3, 8.7, 6.2, 1.9 Hz, 5H), -2.78 (s, 1H).

**8. Preparation of 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (6).** Following the synthesis procedure for 5, the reaction mixture of 4-formylbenzoate (6.0 g, 36 mmol), pyrrole (2.5 mL, 36 mL) in propionic acid (170 mL) afforded the residue, the reaction time is 12 h. Then the residue was purified by column chromatography (silica gel, DCM : ethanol = 99 : 1) to give 6 as a purple powder (1.15 g, 15%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>-*d*, TMS, δ/ppm): 8.81 (s, 8H), 8.43 (d, 8H), 8.28 (d, 8H), 4.11 (s, 12H), 2.83 (s, 2H).

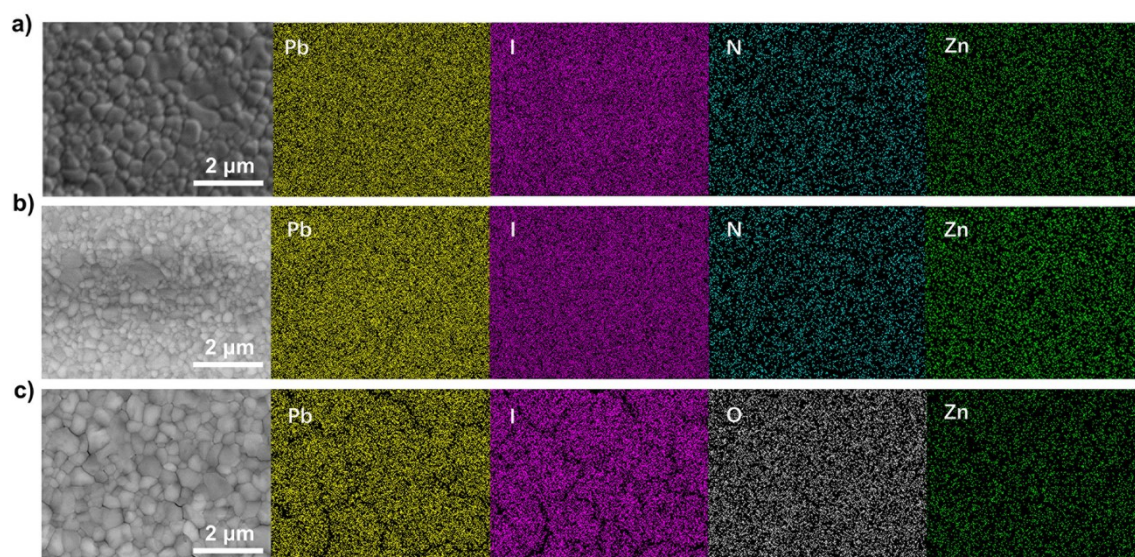
**9. Preparation of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (7).** A mixture of 6 (450 mg, 0.6 mmol) and 2 M KOH solution (20 mL) in THF (30 mL) was refluxed for 48 h under air atmosphere. The reaction was checked by thin-layer chromatography (TLC). After the reaction, the mixture solution was slowly treated with dilute HCl solution to pH = 3. Then the residue was filtrated and washed with deionized water to give 8 as a purple powder (390 mg, 82%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, TMS, δ/ppm): 8.87 (s, 4H), 8.37 (q, *J* = 8.1 Hz, 8H), -2.94 (s, 2H).



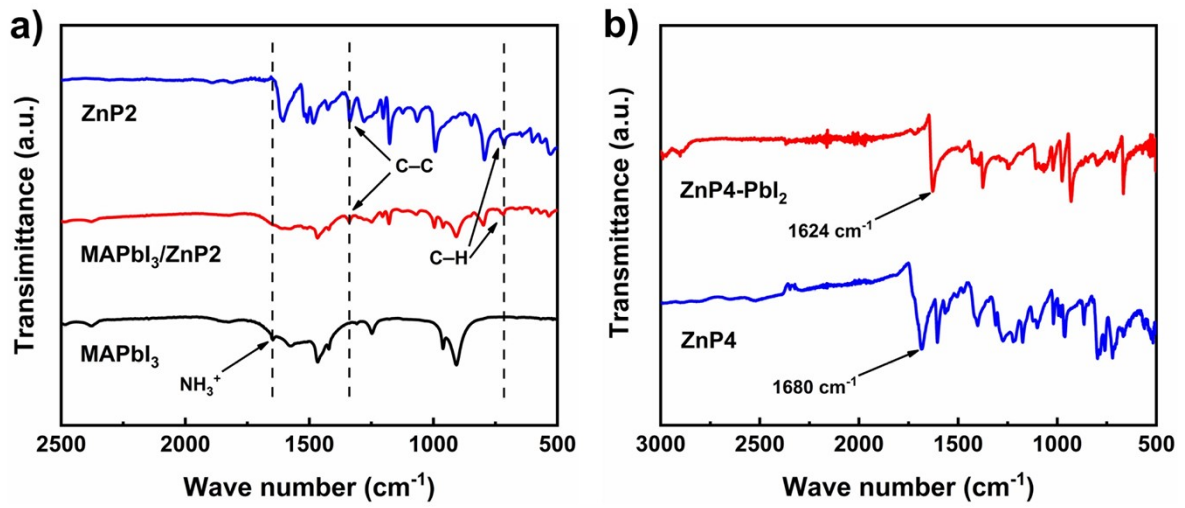
**Scheme S1.** Synthesis of ZnP1, ZnP2, ZnP3, and ZnP4.



**Figure S1.** SEM images of MAPbI<sub>3</sub> films modified by different content of ZnPI (a) 0.01% and (b) 0.1%.

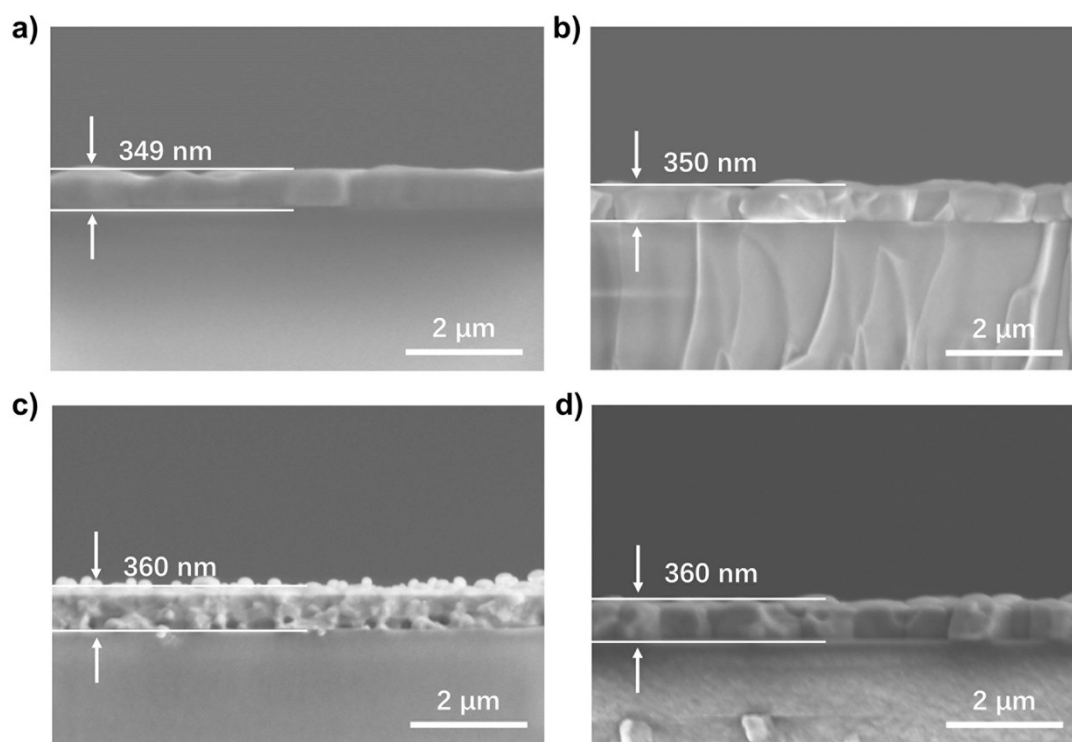


**Figure S2.** Elemental mapping images for (a) ZnP1, (b) ZnP2, and (c) ZnP3-modified MAPbI<sub>3</sub> films.

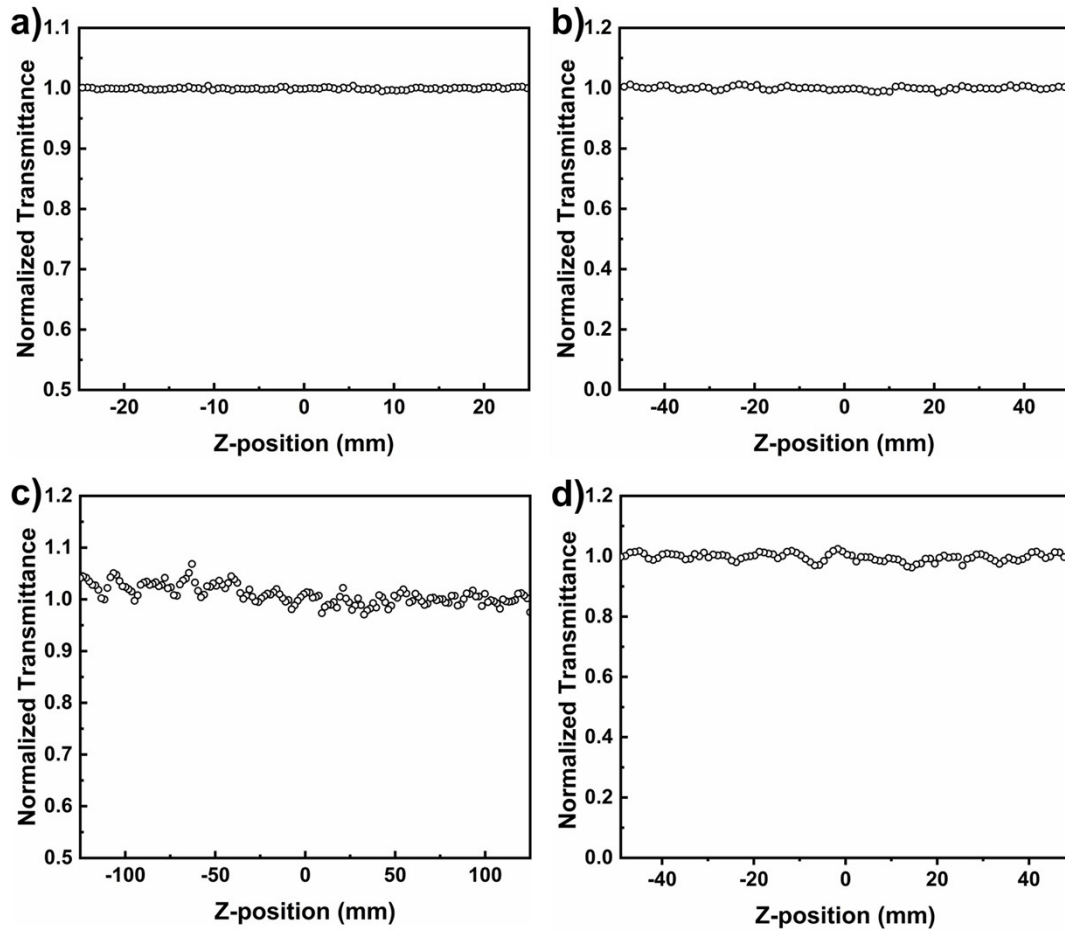


**Figure S3.** (a) FTIR spectra of MAPbI<sub>3</sub>, MAPbI<sub>3</sub>/ZnP2, and ZnP2. (b) FTIR spectra of ZnP4 and ZnP4-PbI<sub>2</sub> mixture.

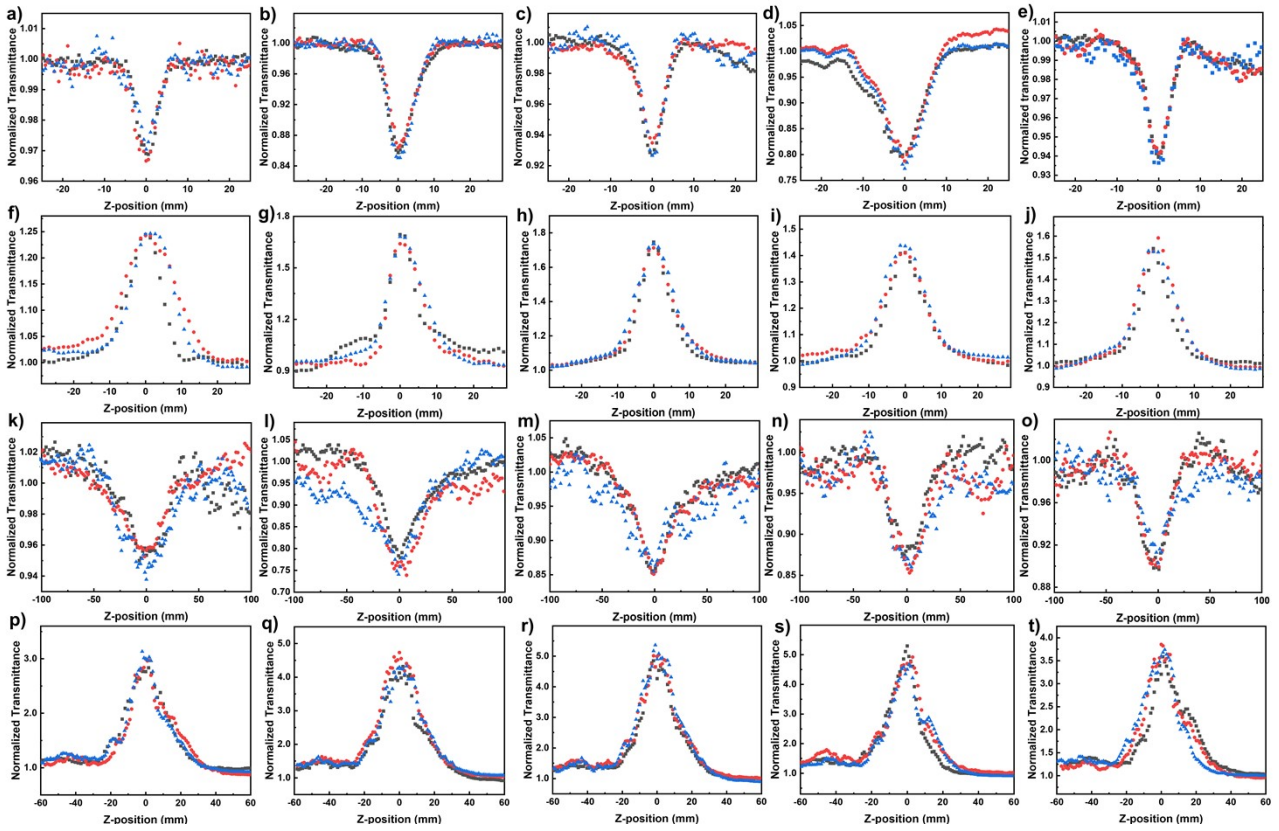




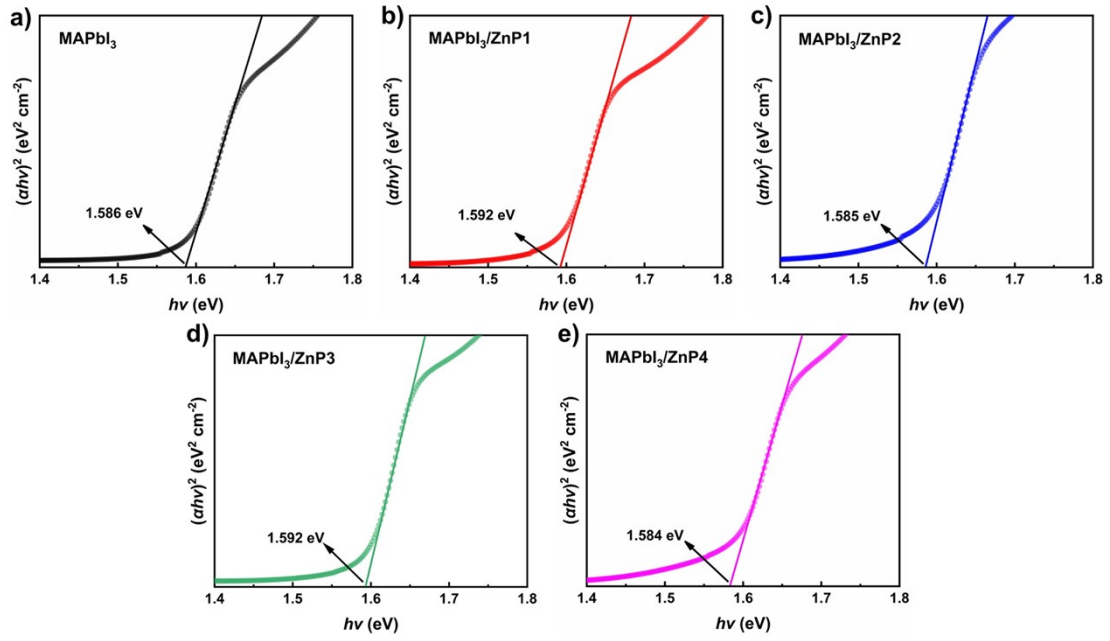
**Figure S4.** Cross-sectional SEM images of MAPbI<sub>3</sub> films (a) without and with (b) ZnP1, (c) ZnP2, and (d) ZnP4 passivation.



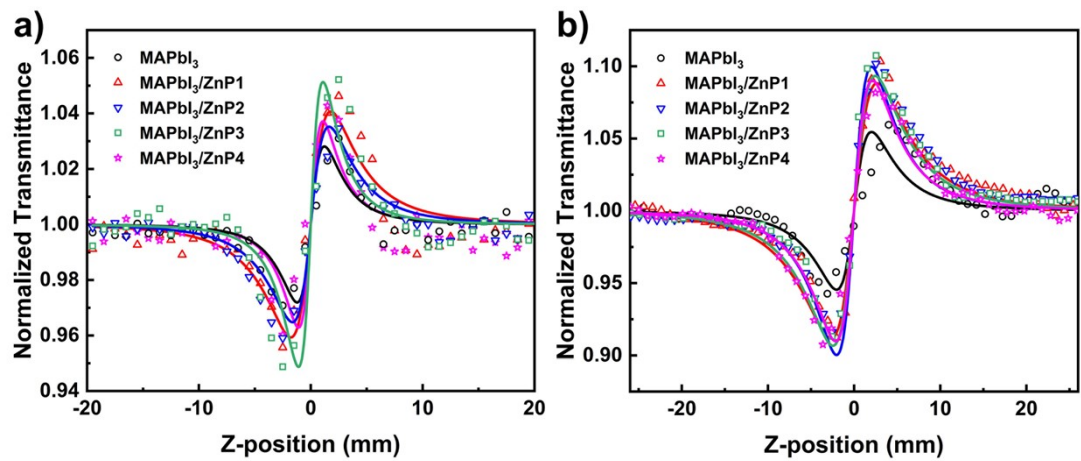
**Figure S5.** Open-aperture Z-scan curves for glass substrates at (a) 800 nm and (b) 515 nm with 34 fs pulse width, and (c) 1064 nm and (d) 532 nm with 15 ns pulse width.



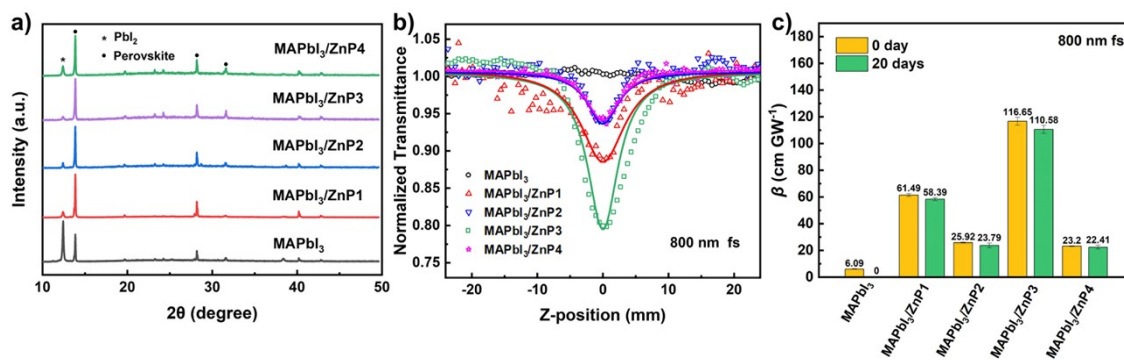
**Figure S6.** Open-aperture Z-scan curves measured at different positions of MAPbI<sub>3</sub> films without and with ZnP1, ZnP2, ZnP3, and ZnP4 passivation using fs pulsed laser at (a)-(e) 800 and (f)-(j) 515 nm, and ns pulsed laser at (k)-(o) 1064 and (p)-(t) 532 nm.



**Figure S7.** The corresponding  $E_g$  values calculated by Tauc plots of (a) the pristine MAPbI<sub>3</sub>, (b) MAPbI<sub>3</sub>/ZnP1, (c) MAPbI<sub>3</sub>/ZnP2, (d) MAPbI<sub>3</sub>/ZnP3, and (e) MAPbI<sub>3</sub>/ZnP4 films.



**Figure S8.** Closed-aperture Z-scan curves of MAPbI<sub>3</sub> films without and with different porphyrins passivation under (a) fs laser excitation at 800 nm and (b) ns laser excitation at 532 nm.



**Figure S9.** (a) XRD patterns and (b) Z-scan curves of corresponding perovskite films without encapsulation after aging in air with the relative humidity of 40% for 20 days. (c) The comparison of the  $\beta$  values for the corresponding perovskite films at 0 day and 20 days.

**Table S1.** Comparison of  $\beta$  values of porphyrin-modified perovskite materials in our work with the literature values.

Materials	Morphology	$\beta$ (cm GW <sup>-1</sup> )	Determination method	Ref.
MAPbI <sub>3</sub>	Film	(5±1.2)×10 <sup>-4</sup>	800 nm, fs	S1
		-6.0±2.0×10 <sup>3</sup>	1064 nm, ns	S2
		-152×10 <sup>3</sup>	532 nm, ps	S3
		-2.25×10 <sup>3</sup>	1064 nm, ps	
		1.1-1.5×10 <sup>3</sup>	1064 nm, ns	S4
		7×10 <sup>3</sup>	1064 nm, ns	S5
CsPbBr <sub>3</sub>	Nanocrystal	-1620×10 <sup>3</sup>	532 nm, ns	S6
	Nanosheet	0.04×10 <sup>3</sup>	514 nm, fs	S7
MAPbBr <sub>3</sub>	Single crystal	0.097	800 nm, fs	
		4.73	800 nm, fs	S9
FAPbBr <sub>3</sub>	Nanocrystal	8.6±0.5	800 nm, fs	S10
CdSe/ZnS QDs	Film	0.0042	800 nm	
		1,98	800 nm, fs	S11
MoS <sub>2</sub>	Solution	1.54	800 nm, fs	S12
		-9.94	532 nm, ns	
MoS <sub>2</sub> -CHT	Solution	8.25	1064 nm, ns	S13
Black phosphorus	Solution	-5.33	532 nm, ns	
Porphyrin-modified MAPbI <sub>3</sub>	Film	23.20-116.65	800 nm, fs	This work
		-157.42-237.32	515 nm, fs	
		6.38-21.61×10 <sup>3</sup>	1064 nm, ns	
		1.48-1.80×10 <sup>7</sup>	532 nm, ns	

**Table S2.** Summary of the NLO refractive parameters of the perovskite film samples.<sup>a</sup>

Samples	Laser	$\lambda$ (nm)	$L$ (nm)	$n_2$ (cm <sup>2</sup> GW <sup>-1</sup> )
MAPbI <sub>3</sub>	34 fs	800	349	$(1.29 \pm 0.12) \times 10^{-3}$
	15 ns	532		$21.32 \pm 1.48$
MAPbI <sub>3</sub> /ZnP1	34 fs	800	350	$(2.78 \pm 0.19) \times 10^{-3}$
	15 ns	532		$52.79 \pm 1.43$
MAPbI <sub>3</sub> /ZnP2	34 fs	800	360	$(2.35 \pm 0.13) \times 10^{-3}$
	15 ns	532		$47.69 \pm 1.69$
MAPbI <sub>3</sub> /ZnP3	34 fs	800	357	$(2.89 \pm 0.24) \times 10^{-3}$
	15 ns	532		$47.03 \pm 1.59$
MAPbI <sub>3</sub> /ZnP4	34 fs	800	360	$(1.69 \pm 0.19) \times 10^{-3}$
	15 ns	532		$44.63 \pm 1.49$

<sup>a</sup> $n_2$ : nonlinear refractive index.



## References

- S1. R. A. Ganceev, K. S. Rao, Z. Yu, W. Yu, C. Yao, Y. Fu, K. Zhang and C. Guo, *Opt. Mater. Express*, 2018, **8**, 1472-1483.
- S2. J. Serna, J. I. Alzate, E. Rueda, D. Ramirez, F. Jaramillo, J. Osorio and H. Garcia, *arXiv*, 2018, preprint, arXiv:1807.06703, <https://doi.org/10.48550/arXiv.1807.06703>.
- S3. R. Zhang, J. Fan, X. Zhang, H. Yu, H. Zhang, Y. Mai, T. Xu, J. Wang and H. J. Snaith, *ACS Photonics*, 2016, **3**, 371-377.
- S4. I. Suárez, M. Vallés-Pelarda, A. F. Gualdrón-Reyes, I. Mora-Seró, A. Ferrando, H. Michinel, J. R. Salgueiro and J. P. M. Pastor, *APL Mater.*, 2019, **7**, 041106.
- S5. C. Redondo-Obispo, I. Suárez, S. J. Quesada, T. S. Ripolles, J. P. Martínez-Pastor, A. L. Álvarez, A. de Andrés and C. Coya, *J. Phys. Chem. Lett.*, 2020, **11**, 2188-2194.
- S6. B. S. Kalanoor, L. Gouda, R. Gottesman, S. Tirosh, E. Haltzi, A. Zaban and Y. R. Tischler, *ACS Photonics*, 2016, **3**, 361-370.
- S7. Y. Wang, X. Li, X. Zhao, L. Xiao, H. Zeng and H. Sun, *Nano Lett.*, 2016, **16**, 448-453.
- S8. J. Zhang, T. Jiang, X. Zheng, C. Shen and X. a. Cheng, *Opt. Lett.*, 2017, **42**, 3371-3374.
- S9. G. Walters, B. R. Sutherland, S. Hoogland, D. Shi, R. Comin, D. P. Sellan, O. M. Bakr and E. H. Sargent, *ACS Nano*, 2015, **9**, 9340-9346.
- S10. L. Yang, K. Wei, Z. Xu, F. Li, R. Chen, X. Zheng, X. Cheng and T. Jiang, *Opt. Lett.*, 2018, **43**, 122-125.
- S11. F. Todescato, I. Fortunati, S. Gardin, E. Garbin, E. Collini, R. Bozio, J. J. Jasieniak, G. Della Giustina, G. Brusatin, S. Toffanin and R. Signorini, *Adv. Funct. Mater.*, 2012, **22**, 337-344.
- S12. F. Gan, N. Dong, Z. Liu, H. Jia, J. Wang and Y. Chen, *Bull. Chem. Soc. Jpn.*, 2020, **93**, 26-31.
- S13. M. Shi, S. Huang, N. Dong, Z. Liu, F. Gan, J. Wang and Y. Chen, *Chem. Commun.*, 2018, **54**, 366-369.