Electronic Supplementary Information

Water-Stable Zero-Dimensional Hybrid Zinc Halide Modulated by π-π Interactions: Efficient Blue Light Emission and Third-Order Nonlinear Optical Response

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Materials

All chemical reagents were purchased from commercial supply without further purification. $ZnCl_2$ (99.99%), 1,2-di(4-pyridyl)ethylene (DPE, 99.9%), hydrochloric acid (HCl, 37%), ethanol (EtOH, AR).

Synthesis of [DPE]$ZnCl_4$

DPE (91.1 mg, 0.5 mmol) and $ZnCl_2$ (68.2 mg, 0.5 mmol) were dissolved in a mixed solution of EtOH (1.5 mL), H_2O (1 mL) and hydrochloric acid (0.5 mL). The suspension was constantly transferred into a 15 mL pressure-resistant bottle, which was then sealed and heated at constant temperature of 150 °C for 24 h. After the reaction, lots of colorless needle crystals were filtrated from the vial and washed with EtOH three times (yield: 85% based on Zn). The structure was subsequently determined to be $C_{12}H_{14}N_2OZnCl_4$ by using the single crystal X-ray diffraction. Elemental analysis calculated (%) for $C_{12}H_{14}N_2OZnCl_4$: C, 35.20; H, 3.45; N, 6.84; Found (%): C, 35.38; H, 3.39; N, 6.78.

Characterizations

Power X-ray diffraction (PXRD) patterns of the samples were recoeded by a Rigaku Dmax 2500 X-ray diffractometer with Cu $K\alpha$ radiation (λ = 1.54056 Å). Elemental analysis of C, H, N was performed on a Vario EL-Cube. Thermal gravimetric analysis (TGA) was performed on a Netzsch STA448F3 thermal analyzer. Ultraviolet-visible (UV-vis) absorption spectrum was carried out on a Lambda950 diffuse Reflectometer. Photoluminescence spectroscopy measurements were measured on an Edinburgh FLS1000 fluorescence spectrometer at room temperature. The time-resolved decay data were carried out using the Edinburgh FLS1000 fluorescence spectrometer with a picosecond pulsed diode laser. The PLQY measurement was performed on an Edinburgh FLS1000 steady state/transient state fluorescence spectrometer with an integrating sphere ($BaSO_4$ coating as reference material) using single photon counting mode. The PLQY was calculated based on the equation: $\eta_{QE} = I_S/(E_R\text{-}E_S)$, which I_S represents the luminescence emission spectrum of the sample, E_R is the spectrum of the excitation light from the empty integrated sphere ($BaSO_4$ coating), and E_S is the excitation spectrum for exciting the sample.

X-ray Crystallography

Single crystal X-ray diffraction (SCXRD) data were obtained on a Synergy Custom with Cu $K\alpha$ radiation at 100 K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with the Olex2 software[1]. All the non-hydrogen atoms were refined with anisotropic temperature parameters and hydrogen atoms were positioned geometrically and refined isotropically. Crystallographic details were presented in Table S2 and some selected bond lengths, bond angles and

H-bonds are listed in Tables S3-S5. CCDC (number of 2355212) contains the supplementary crystallographic data for this paper.

Preparation of [DPE]$ZnCl_4$@PDMS samples

The polydimethylsiloxane (PDMS) films were obtained using Sylgard 184 (Dow Corning) by thoroughly mixing 10 parts bases with 1 part curing agent. The fully ground [DPE]$ZnCl_4$ sample was added to the PDMS mixture and stirred for three hours to form [DPE]$ZnCl_4$ -dispersed PDMS suspension. Then the mixed suspension was added to a round mold, and then the template was placed in a vacuum oven at 60 °C for 6 h to prepare transparent and flexible [DPE]$ZnCl_4$ @PDMS samples.

Third-order Nonlinear Optical Measurements

The third-order nonlinear optical property of samples was tested using the Z-scan technique with an output wavelength of 532 nm. All the measurements were conducted at room temperature. The excitation light source was an Nd: YAG laser with a repetition frequency of 10 Hz.

$$T(Z, S=1) = \frac{1}{\sqrt{\pi} q_0(Z,0)} \int_{-\infty}^{\infty} \ln\left[1 + q_0(Z,0) e^{-r^2}\right] dr$$

$$q_0(Z,0) = \beta I_0 L_{eff}$$

$$L_{eff} = [1 - exp(-\alpha l)]/\alpha$$

In these equations, I_0 is the on-axis peak intensity at the focus (Z = 0), L_{eff} is the effective thickness of the sample, l is the sample thickness, and α_0 is the linear absorption coefficient. By fitting the curves, the nonlinear absorption coefficient β was obtained.

Theoretical band calculation

The SCXRD data of [DPE]$ZnCl_4$ was directly used to calculate its electronic structure in Castep software. The total energy was estimated with density functional theory (DFT) using Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)[2]. Hence, the C-$2s^2 2p^2$, N-$2s^2 2p^3$, H-$1s^1$, Cl-$3s^2 3p^5$, and Zn-$3d^{10} 4s^2$ orbitals were adopted as valence electrons. The number of plane wave included in the basis sets was determined by a cutoff energy of 320 eV and numerical integration of the Brillouin zone is performed using Monkhorst-Pack k-point sampling of 2×2×2. Other calculating parameters and convergence criteria were set by the default values of the CASTEP code.

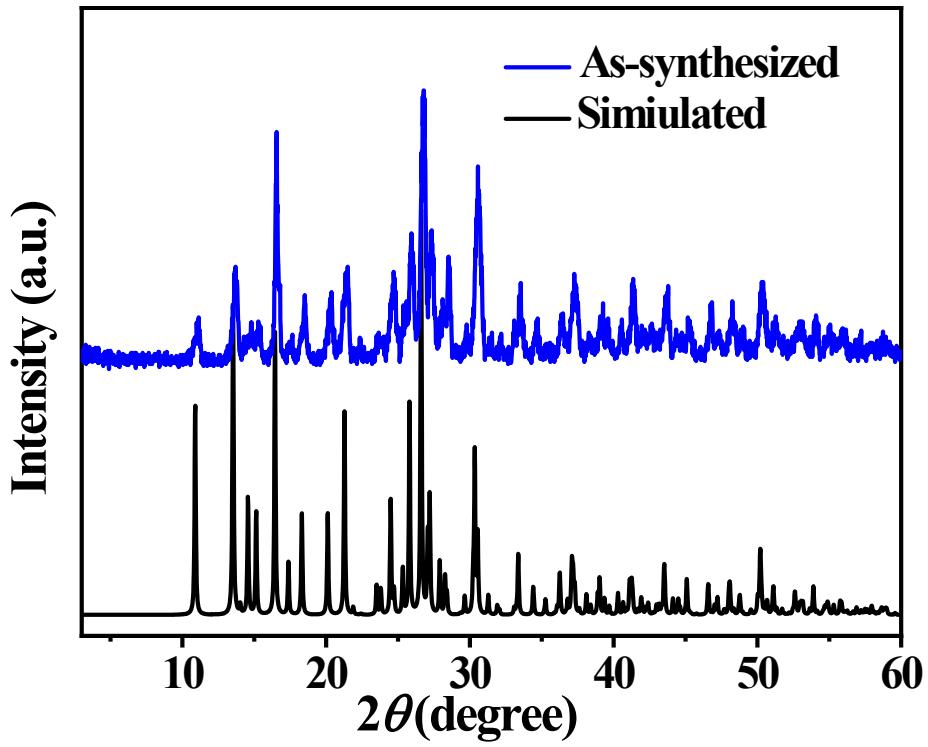

Fig. S1 The simulated and experimental PXRD patterns of [DPE]$ZnCl_4$.

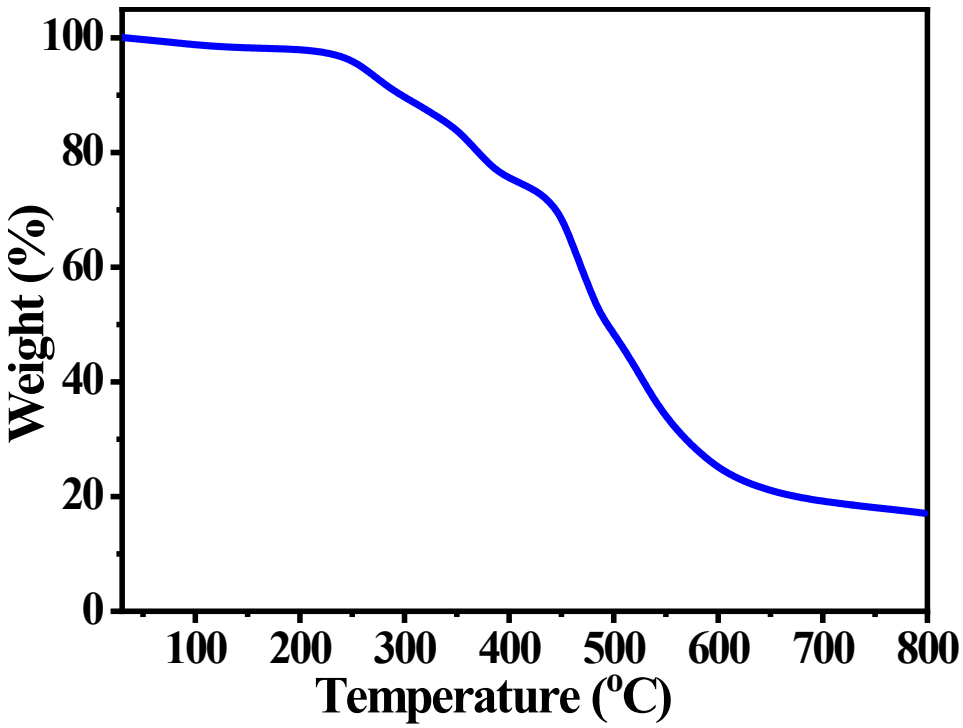

Fig. S2 Thermogravimetric curves of [DPE]$ZnCl_4$.

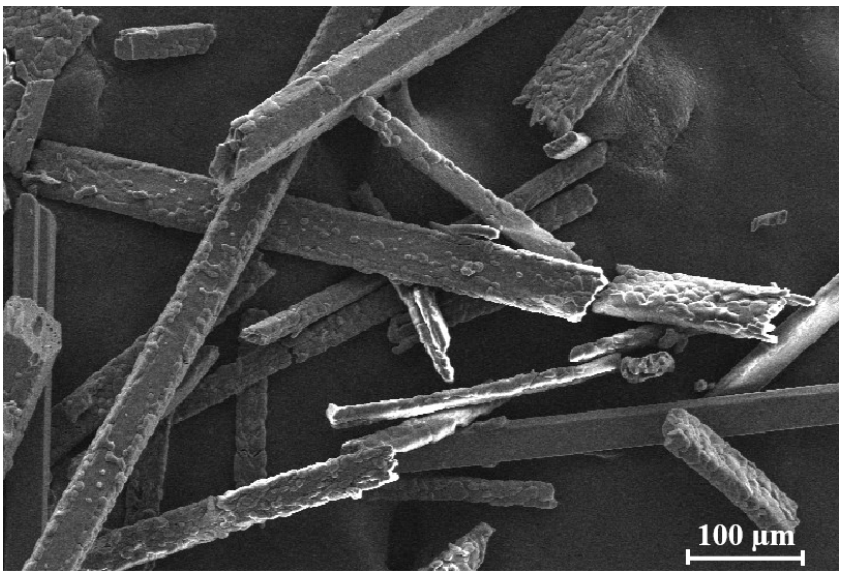

Fig. S3 The SEM image of compound [DPE]$ZnCl_4$.

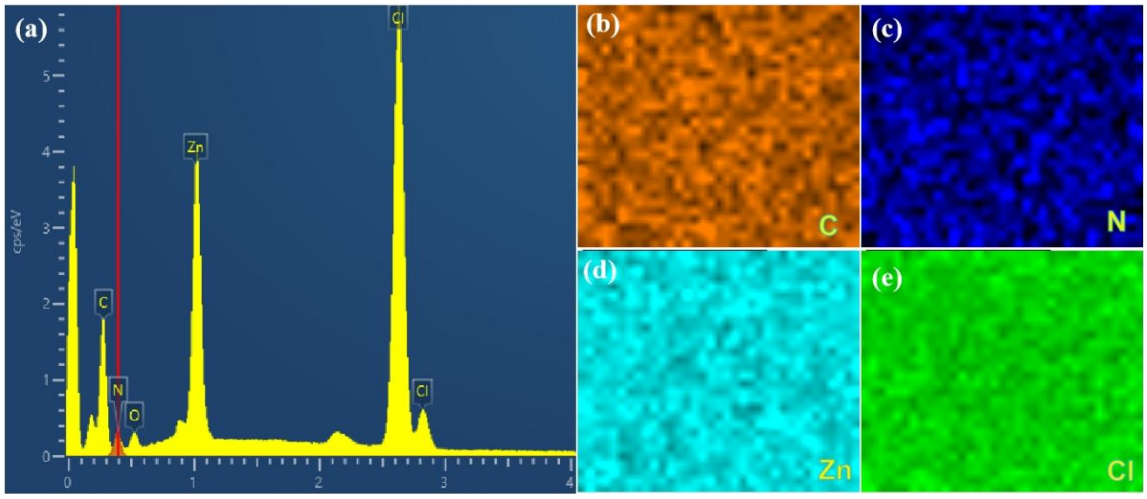

Fig. S4 The EDS (a) and elemental mapping images (b-e) of [DPE]$ZnCl_4$.

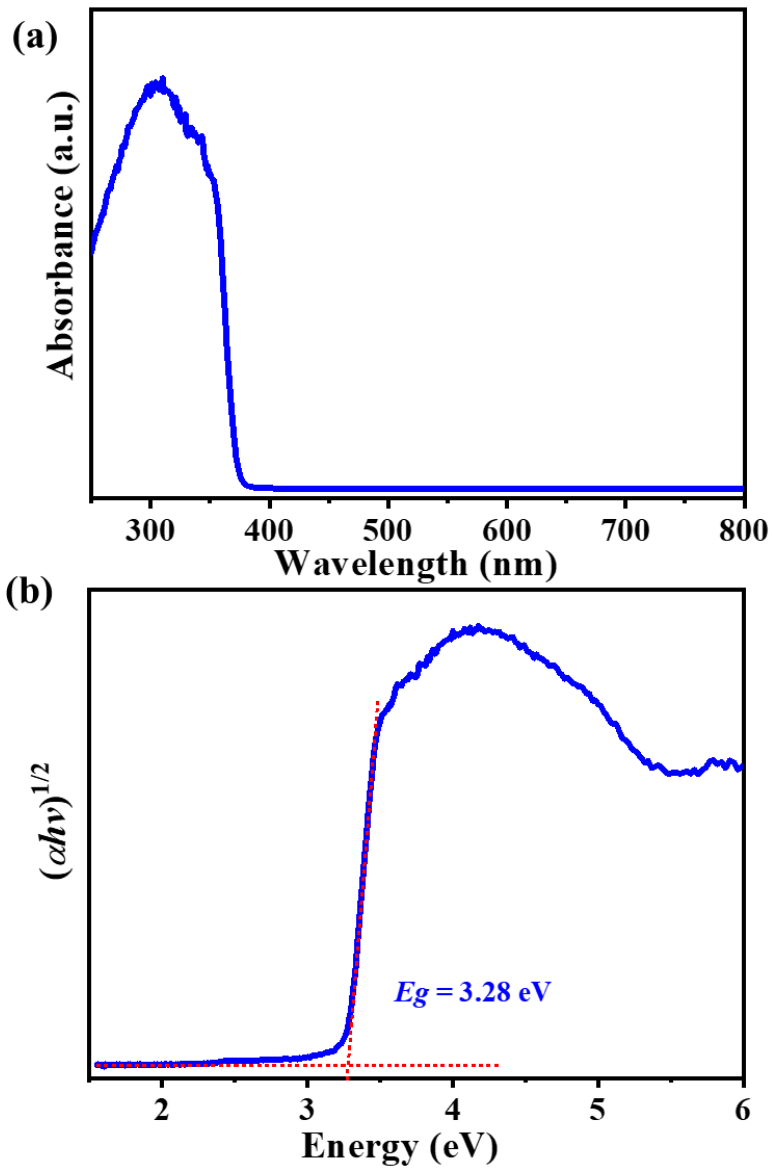

Fig. S5 UV-vis absorption spectrum (a) and band gap (b) of $[DPE]ZnCl_4$.

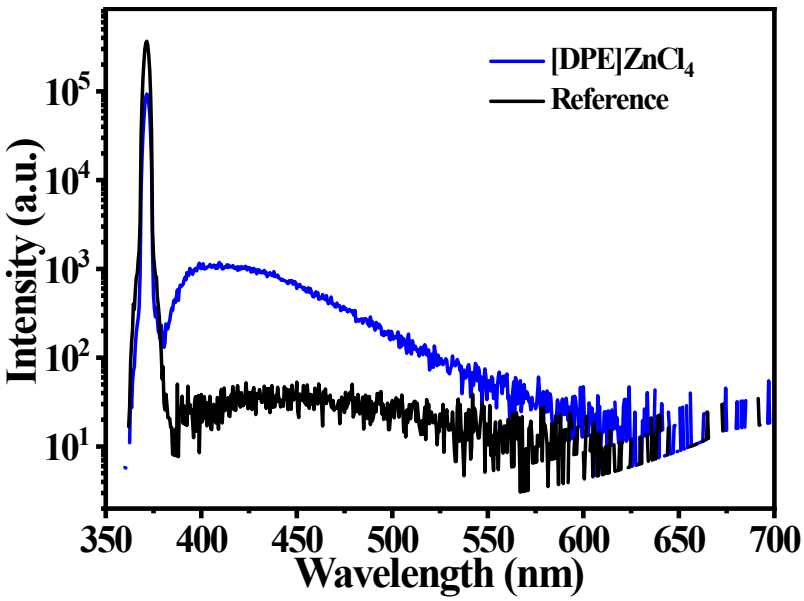

Fig. S6 The PLQY of blue light emission excited by 370 nm UV light for $[DPE]ZnCl_4$.

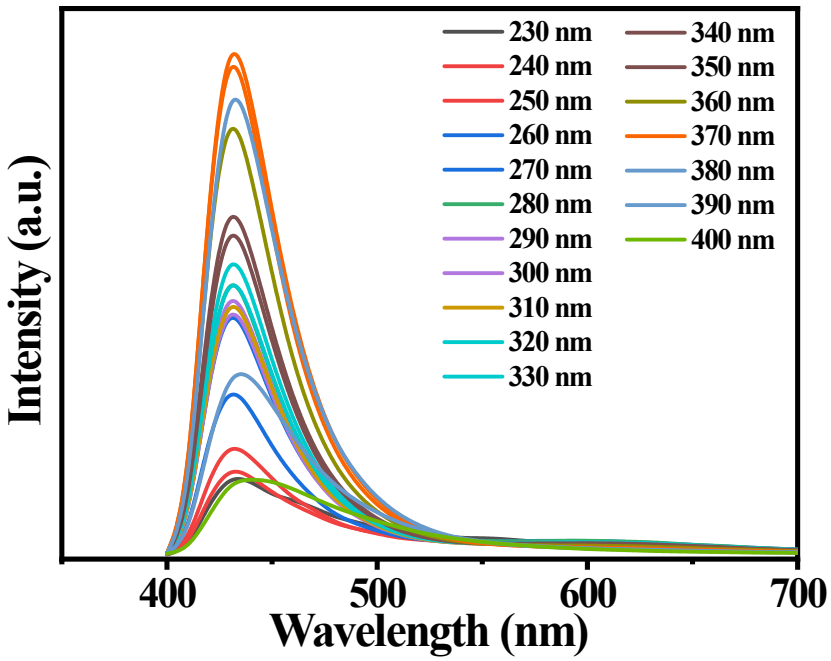

Fig. S7 The emission wavelength dependent PL excitation spectrum of $[DPE]ZnCl_4$.

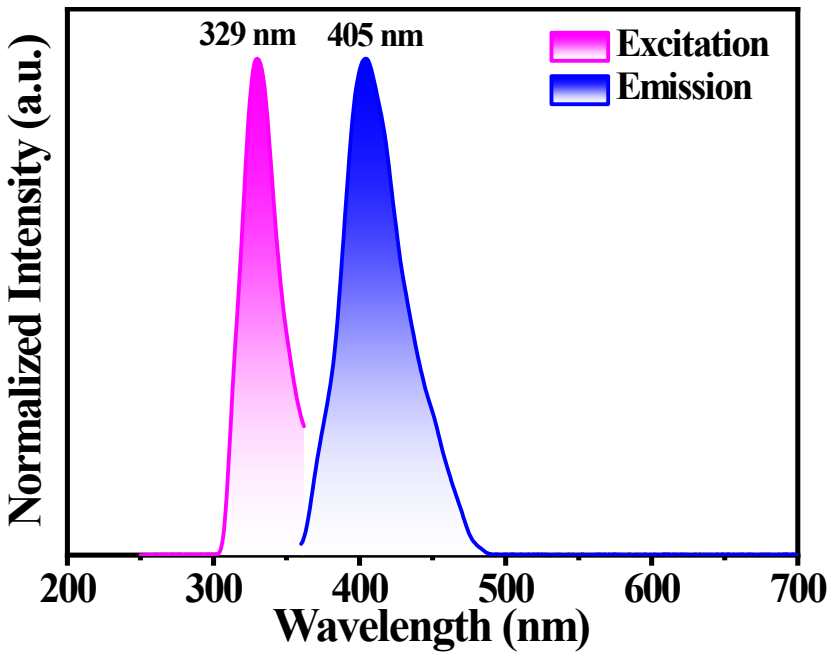

Fig. S8 The excitation and emission spectra of $[DPE]Cl_2$.

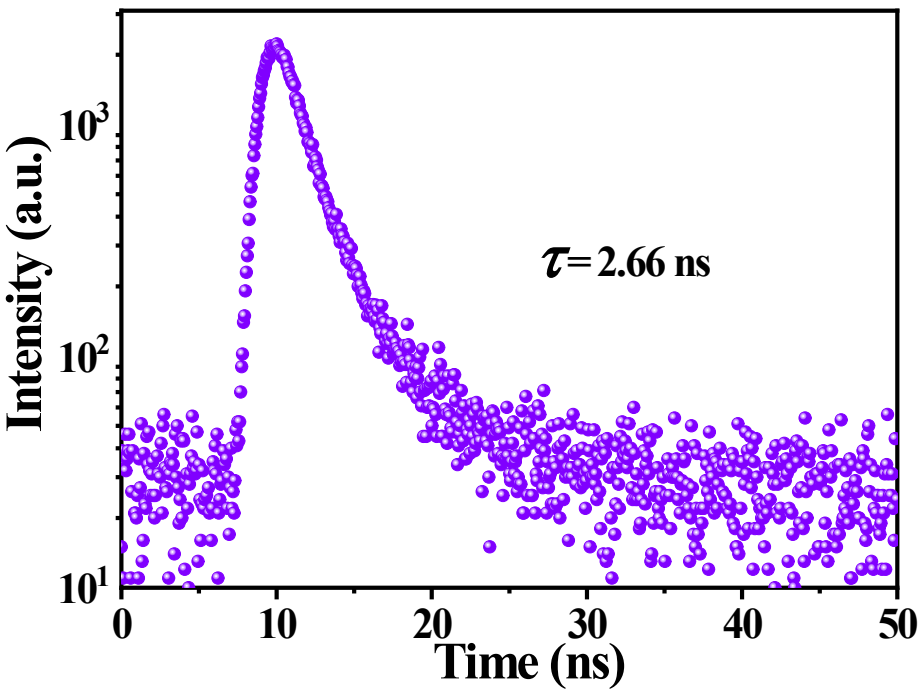

Fig. S9 The PL decay curve at 405 nm at 300K of $[DPE]Cl_2$.

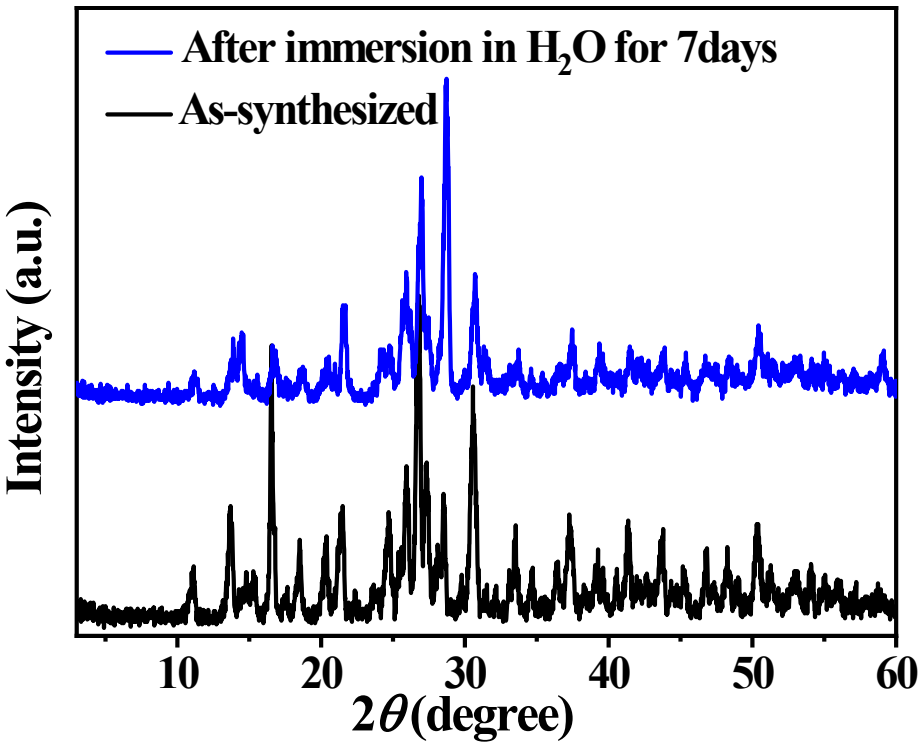

Fig. S10 The PXRD patterns of [DPE]$ZnCl_4$ before and after immersion in water for 7 days.

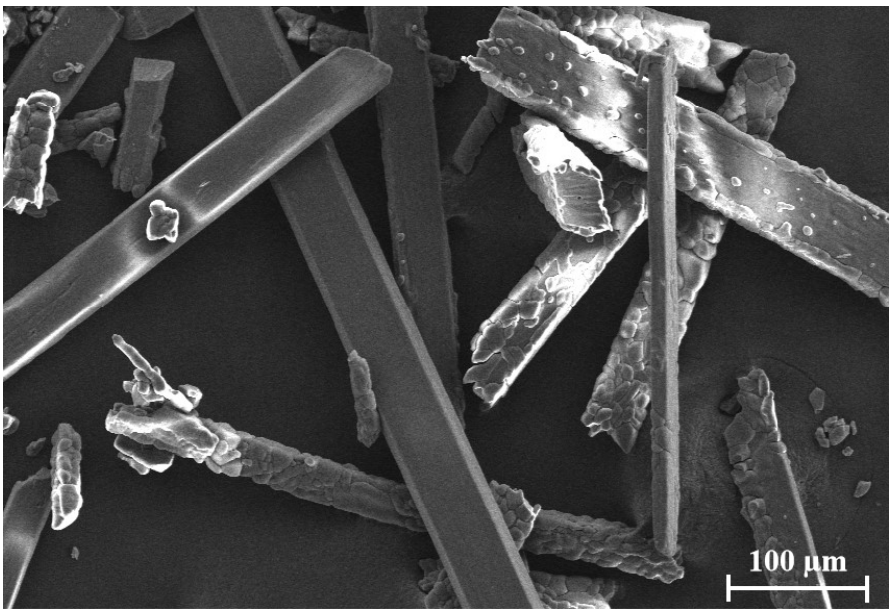

Fig. S11 The SEM image of [DPE]$ZnCl_4$ after immersion in water for 7 days.

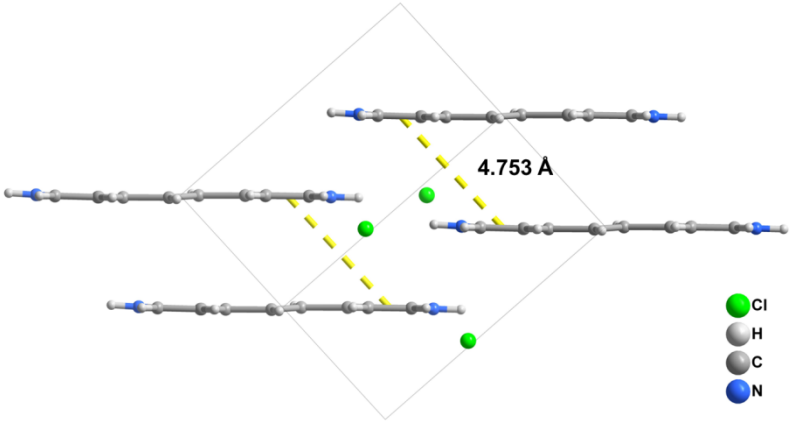

Fig. S12 Crystal structure and the π-π interaction in the organic salt of [DPE]Cl. (The crystal structure is cited from the Cambridge Crystallographic Data Centre with the refcode of DANGOR)

Table S1 Summary of the third-order NLO properties of metal halide perovskite materials and other crystalline materials.

Compounds	**Method**	T_{min}	β (10^{-10} m W^{-1})	**Reference**
[DPE]$ZnCl_4$	**PDMS film**	**0.70**	**3.81**	***This work***
[DPE]Cl_2		**0.95**	**0.52**	
$MAPbBr_3$ QDs (5 nm)	solution	0.972	0.418	*Adv. Opt. Mater.*, **2016**, *4*, 1732–1737.
$CsPbCl_3$ NCs (15.2 nm)	solution	0.84	0.00136	*J. Alloys Compd.*, **2017**, *724*, 889–896.
$CsPbBr_3$ NCs (21.4 nm)	solution	0.56	0.00322	
$CsPbI_3$ NCs (28.7 nm)	solution	0.83	0.00154	
$FAPbBr_3$ NCs (15 nm)	solution	/	0.042	*Opt. Lett.*, **2018**, *43*, 122–125.
$CsPbBrI_2$ QDs (12.4 nm)	solution	/	0.95	*Opt. Mater.*, **2018**, *75*, 880–886.
Ni-Doped $CsPbBr_3$	solution	0.81	1	*J. Phys. Chem. Lett*., **2019**, *10*, 5577–5584.
Au–$CsPbBr_3$ NCs (9.45 nm)	solution	/	2.34	*J. Mater. Sci.*, **2020**, *55*, 10678–10688.
$CsPbBr_3$ QD film (10 nm)	film	0.85	0.279	*Nanoscale*, **2018**, *10*, 22766–22774.
AlOC-92	PDMS film	0.917	0.75	*Aggregate*. **2023**, *4*, e264.
AlOC-90		0.862	1.35	
AlOC-93		0.587	7.18	
AlOC-94		0.715	4.12	
$(TBA)_3[VMo_5O_{19}]$	glasses	0.75	0.60	*Inorg. Chem. Front.* **2022**, *9*, 4413-4424
$(TBA)_4[V_8Mo_2O_{28}] \cdot CH_3CN$		0.5	1.24	
$(TBA)_4[HV_9MoO_{28}] \cdot 2CH_3CN$		0.06	6.92	
$[(Tp^*WS_3Cu_3)_2(Btta)_3]$	DMF	0.71	0.002	*Inorg. Chem.* **2017**, *56*, 5669-5679.
$\{[Bu_4N][WS_4Cu_3(CN)_2]\}_n$	DMF	~ 0.68	0.75	*Cryst. Growth Des.* **2008**, *8*, 389-390
$\{[Zn_2(L)_2(H_2O)_4] \cdot 2DMA \cdot 2H_2O\}$	DMSO	~ 0.93	0.053	*Sci China Mater* **2021**, *64*, 408-419.
$[NH_4][WS_4Cu_4(dpypy)Cu(CN)_4] \cdot DMF$	DMF	0.8	0.8	*Cryst. Growth Des.* **2021**, *21*, 3225-3233.

[(Tp*$WS_3Cu_2Cl)_2$(dppe)]	DMF	0.84	0.0037	*Inorg. Chem.* **2016**, *55*, 1861-1871.
[(Tp*WS_3Cu_4(μ_4-Cl) (μ-Cl)$(dppp)_2$]PF_6		0.15	0.026	
[Tp*WS_3Cu_2(HMT)]$_2(PF_6)_2$	DMF	0.88	0.4	*Chin. J. Chem.* **2021**, *39*, 647-654.
[PPh_4] (η^5-C_5Me_5)$MoS_3(CuBr)_3$	aniline	~ 0.76	0.708	*Inorg. Chem.* **2008**, *47*, 5332-5346.
(η^5-C_5Me_5)MoS_3Cu_3(μ-bpp)(μ-Br)Br		~ 0.72	0.488	
[PPh_4] (η^5-C_5Me_5)$MoS_3(CuNCS)_3$	aniline	~ 0.74	0.758	*Inorg. Chem.* **2007**, *46*, 6647-6660.
[Tp*$WS_3Cu_2(L^a)]_4(BF_4)_4$	DMF	0.37	0.7	*Research.* **2022**, 9819343.
[Tp*$WS_3Cu_2(L^a)]_6(SbF_6)_6$		0.34	0.9	

Table S2 Crystal data and structure refinements for [DPE]$ZnCl_4$.

Compound	[DPE]$ZnCl_4$
chemical formula	$C_{12}H_{14}Cl_4N_2OZn$
Fw	409.42
Space group	*C*2/*c*
a (Å)	7.60570(10)
b (Å)	13.10570(10)
c (Å)	16.3610(2)
α (°)	90
β (°)	97.2170(10)
γ (°)	90
V (Å^3)	1617.91(3)
Z	4
D_{calcd} (g · cm^{-3})	1.681
Temp (*K*)	293(2)
μ (mm^{-1})	8.156
F (000)	824.0
Reflections collected	15019
GOF	1.067
[a]R_1, wR_2 ($I > 2\sigma(I)$)	0.0178/0.0473
[b]R_1, wR_2 (all data)	0.0183/0.0476

[a]$R_1 = \sum||F_o| - |F_o||/\sum|F_o|$. [b]$wR_2 = [\sum w (F_o^2 - F_c^2)^2/\sum w (F_o^2)^2]^{1/2}$.

Table S3 Selected bond lengths (Å) and bond angles (°) for $[DPE]ZnCl_4$.

Zn1-Cl1[1]	2.2693(3)	Zn1-Cl2[1]	2.2812(4)
Zn1-Cl1	2.2693(3)	Zn1-Cl2	2.2812(4)
Cl1[1]-Zn1-Cl1	110.291(19)	Cl1[1]-Zn1-Cl2[1]	108.317(12)
Cl1[1]-Zn1-Cl2	109.182(12)	Cl1-Zn1-Cl2[1]	109.185(12)
Cl1-Zn1-Cl2	108.318(12)	Cl2-Zn1-Cl2[1]	111.55(2)

Symmetry code: [1]1-X, +Y, 1/2-Z; [2]1-X, 2-Y, 1-Z

Table S4 The list of hydrogen bonds in [DPE]$ZnCl_4$.

D-H···A	d(D-H)	d(H···A)	<(DHA)
N1—H1···Cl2	2.82	3.493	135.8
N1—H1···O1	2.09	2.806	140
O1—H1B···Cl1	2.31	3.158	178
O1—H1C···Cl1	2.43	3.158	143
O1—H1C···Cl2	2.79	3.322	122
C6—H6···Cl1	2.81	3.670	155

References

[1] G. M. Sheldrick, SHELXT-Integrated Space-Group and Crystal-Structure Determination, *Acta Cryst.*, **2015**, *A71*, 3-8.

[2] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys. Condens. Matter.* **2002**, *14*, 2717.