Electronic Supplementary Information (ESI) for

Crystal clear: unveiling giant birefringence in organic-inorganic cocrystals

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Table S1. Crystallographic data for **Li-4HP**, **Li-4HP2**, and **Mg-4HP**.

	Li-4HP	**Li-4HP2**	**Mg-4HP2**
Temperature/K	171.00	140	293.00
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$I2/a$
a/Å	8.821(8)	8.2120(6)	24.6517(11)
b/Å	10.477(9)	8.9624(6)	6.4107(3)
c/Å	9.205(9)	9.9320(7)	26.2782(12)
α/°	90	82.101(2)	90
β/°	110.89(3)	68.227(2)	106.673(2)
γ/°	90	70.184(2)	90
Volume/Å^3	794.8(13)	638.59(8)	3978.3(3)
Z	4	1	8
ρ_{calc} g/cm^3	1.522	1.441	1.491
μ/mm^{-1}	0.134	0.119	0.166
F(000)	376.0	288.0	1872.0
Crystal size/mm^3	0.216 × 0.126 × 0.098	0.289 × 0.21 × 0.178	0.271 × 0.242 × 0.152
Radiation	MoKα (λ = 0.71073)		
2θ range for data collection/°	5.494 to 54.966	4.832 to 56.634	5.366 to 55.148
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -11 ≤ l ≤ 11	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13	-32 ≤ h ≤ 32, -8 ≤ k ≤ 8, -34 ≤ l ≤ 34
Reflections collected	14271	14595	57494
Independent reflections	1823 [R_{int} = 0.1264, R_{sigma} = 0.0732]	3158 [R_{int} = 0.0502, R_{sigma} = 0.0377]	4602 [R_{int} = 0.1047, R_{sigma} = 0.0495]
Data/restraints/parameters	1823/1/122	3158/1/184	4602/3/292
Goodness-of-fit on F^2	1.019	1.037	1.176
Final R indexes [I≥2σ (I)]	R_1 = 0.0535, wR_2 = 0.1130	R_1 = 0.0404, wR_2 = 0.1094	R_1 = 0.0843, wR_2 = 0.1705
Final R indexes [all data]	R_1 = 0.0926, wR_2 = 0.1307	R_1 = 0.0454, wR_2 = 0.1133	R_1 = 0.1177, wR_2 = 0.1859
Largest diff. peak/hole / e Å^{-3}	0.24/-0.23	0.43/-0.23	0.30/-0.34

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **Li-4HP**, **Li-4HP2**, and **Mg-4HP**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	$U_{(eq)}$
		Li-4HP		
O1	9047.7(19)	5381.4(16)	3572.2(17)	28.9(4)
O3	7603.2(19)	3744.9(15)	6346.9(18)	30.9(4)
O2	8024(2)	6715.1(16)	6306.6(19)	33.4(5)
O5	5280(2)	2791.3(16)	5495(2)	38.0(5)
O4	5909(2)	4217.4(16)	4077.0(19)	38.3(5)
N2	6250(2)	3583.9(17)	5295(2)	23.9(4)
N1	6097(3)	6038.7(19)	9127(2)	32.2(5)
C1	8122(3)	5596(2)	2175(2)	22.4(5)
C5	8309(3)	4945(2)	890(3)	29.2(6)
C4	7309(3)	5182(2)	9424(3)	34.0(6)
C2	6820(3)	6491(2)	1784(3)	29.1(6)
C3	5860(3)	6693(2)	285(3)	33.5(6)
Li1	8704(5)	5170(4)	5526(4)	28.4(9)
		Li-4HP2		
O5	8019.7(13)	3525.9(12)	3509.4(11)	29.6(2)
O6	86.2(14)	1693.0(10)	729.8(10)	25.7(2)
O2	8981.8(11)	9162.7(10)	2152.5(9)	20.86(19)
O1	8161.1(11)	5499.2(10)	390.3(9)	19.50(19)
O7	9566.9(13)	2152.8(13)	4861.7(10)	32.3(2)
O3	885.3(13)	3339.1(12)	2898.4(10)	29.9(2)
N3	9493.8(14)	3007.7(12)	3771.0(10)	19.9(2)
N4	2557.2(13)	7284.4(12)	1735.3(11)	21.1(2)
N2	3960.0(14)	8516.5(13)	4184.5(11)	23.5(2)
C6	5717.9(16)	200.4(13)	2920.3(12)	19.6(2)
C5	5482.5(15)	7577.0(13)	337.4(12)	18.8(2)
C3	3361.0(16)	5817.0(15)	2179.8(13)	21.1(2)
C11	3600.2(16)	8144.3(14)	825.2(13)	20.8(2)
C9	7211.1(16)	7501.3(14)	3515.4(13)	20.5(2)
C10	7400.9(15)	8967.8(13)	2828.9(11)	15.8(2)
C8	5509.3(17)	7318.1(15)	4160.2(13)	22.9(3)
C7	4053.9(16)	9943.8(15)	3585.6(13)	22.8(2)
C2	5235.1(16)	5179.0(13)	1742.8(12)	18.6(2)
C1	6408.7(15)	6049.1(13)	796.9(11)	15.6(2)
Li1	9869(3)	3823(2)	1118(2)	20.0(4)
		Mg-4HP		

Atom	*x*	*y*	*z*	$U_{(eq)}$
Mg1	5005.5(6)	7407.3(15)	6269.3(5)	24.3(3)
O8	4453.2(11)	2417(4)	7079.5(10)	34.3(6)
O6	4877.3(11)	4567(4)	5892.3(11)	37.9(6)
O1	4813.7(11)	6275(4)	6938.2(10)	34.9(6)
O3	5132.1(12)	10265(4)	6616.9(12)	40.0(7)
O7	5537.5(12)	2451(4)	5403.1(11)	37.2(7)
O4	5198.9(11)	8530(4)	5596.9(10)	36.0(6)
O5	5851.4(11)	6798(4)	6613.0(12)	39.6(7)
O2	4156.8(11)	8045(4)	5927.3(12)	42.0(7)
O9	3333.1(12)	4963(4)	5712.9(13)	49.7(8)
O10	3866.3(13)	2285(4)	5718.7(14)	51.5(8)
O13	6666.3(13)	9958(4)	6760.0(15)	59.7(9)
O12	6126.3(14)	2592(4)	6763.7(16)	59.1(10)
O14	7013.2(13)	3048(5)	6860.0(15)	61.6(9)
N4	3389.2(14)	3022(5)	5676.7(13)	34.6(7)
O11	2974.9(13)	1882(5)	5606.6(15)	62.8(10)
N3	6607.2(14)	1885(5)	6797.9(13)	38.2(8)
N1	7181.1(14)	3949(6)	5579.1(14)	43.0(8)
N2	2807.3(15)	1022(6)	6902.5(15)	49.3(9)
C6	3932.4(15)	1967(6)	7023.2(14)	28.8(7)
C3	6053.7(16)	2922(6)	5451.8(14)	28.7(7)
C2	6261.2(17)	4993(6)	5554.0(16)	38.2(9)
C10	3732.9(17)	9899(6)	6965.4(19)	45.5(10)
C1	6809.8(18)	5445(6)	5611.9(17)	43.9(10)
C7	3523.4(18)	3524(6)	7018.6(18)	46.5(11)
C4	6466.5(18)	1410(6)	5412.3(17)	42.6(10)
C5	7012.0(19)	1967(7)	5478.9(19)	48.6(11)
C9	3180.4(19)	9499(7)	6910(2)	54.8(12)
C8	2977.1(19)	3005(7)	6958(2)	53.7(12)

Table S3. Interatomic distances (Å) for **Li-4HP**, **Li-4HP2**, and **Mg-4HP**.

Atom	Atom	Length	Atom	Atom	Length
		Li-4HP			
O1	C1	1.274(3)	O4	Li1	2.551(5)
O1	Li1[1]	1.945(5)	N1	C4	1.347(3)
O1	Li1	1.940(4)	N1	C3	1.345(3)
O3	N2	1.252(3)	C1	C5	1.425(3)
O3	Li1	2.065(4)	C1	C2	1.426(3)
O2	Li1	1.950(4)	C5	C4	1.347(3)
O5	N2	1.253(3)	C2	C3	1.353(3)
O4	N2	1.244(2)			
[1]2-X,1-Y,1-Z					
		Li-4HP2			
O5	N3	1.2521(13)	N4	C11	1.3514(15)
O5	Li1	2.333(2)	N2	C8	1.3530(17)
O6	Li1	1.935(2)	N2	C7	1.3490(17)
O2	C10	1.2812(13)	C6	C10	1.4276(15)
O1	C1	1.2726(13)	C6	C7	1.3632(16)
O1	Li1	1.942(2)	C5	C11	1.3644(15)
O1	Li1[1]	1.962(2)	C5	C1	1.4289(15)
O7	N3	1.2462(13)	C3	C2	1.3638(16)
O3	N3	1.2529(13)	C9	C10	1.4250(15)
O3	Li1	2.157(2)	C9	C8	1.3612(16)
N4	C3	1.3522(16)	C2	C1	1.4339(15)
[1]2-X,1-Y,-Z					
		Mg-4HP			
Mg1	O6	2.054(3)	N4	O11	1.226(4)
Mg1	O1	2.078(3)	N1	C1	1.346(5)
Mg1	O3	2.031(3)	N1	C5	1.339(6)
Mg1	O4	2.086(3)	N2	C9	1.337(6)
Mg1	O5	2.058(3)	N2	C8	1.333(6)
Mg1	O2	2.067(3)	C6	C10	1.407(5)
O8	C6	1.282(4)	C6	C7	1.416(5)
O7	C3	1.278(4)	C3	C2	1.420(5)
O9	N4	1.259(4)	C3	C4	1.430(5)
O10	N4	1.243(4)	C2	C1	1.348(5)
O13	N3	1.251(4)	C10	C9	1.352(6)
O12	N3	1.248(4)	C7	C8	1.351(6)
O14	N3	1.221(4)	C4	C5	1.353(6)

Table S4. Bond Angles (˚) for **Li-4HP**, **Li-4HP2**, and **Mg-4HP**.

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
			Li-4HP				
C1	O1	Li1	134.44(19)	O1	Li1	O3	132.1(2)
C1	O1	Li1[1]	132.27(18)	O1[1]	Li1	O3	99.79(19)
Li1	O1	Li1[1]	92.46(18)	O1[1]	Li1	O2	119.3(2)
N2	O3	Li1	104.90(17)	O1	Li1	O2	114.6(2)
N2	O4	Li1	81.90(16)	O1	Li1	O4	90.07(16)
O3	N2	O5	119.23(19)	O1[1]	Li1	O4	139.1(2)
O2	Li1	O3	102.64(19)	O1	Li1	O1[1]	87.54(18)
O2	Li1	O4	98.65(18)	O1	C1	C2	122.7(2)
O4	N2	O3	118.90(19)	C5	C1	C2	115.2(2)
O3	Li1	O4	54.25(12)	C4	C5	C1	121.0(2)
O4	N2	Li1	70.70(15)	C5	C4	N1	121.0(2)
C3	N1	C4	121.0(2)	C3	C2	C1	121.0(2)
O1	C1	C5	122.1(2)	N1	C3	C2	120.7(2)
			Li-4HP2				
N3	O5	Li1	85.91(8)	O1	C1	C5	122.05(10)
O7	N3	O5	120.07(10)	O6	Li1	O1[1]	109.61(10)
O7	N3	O3	121.39(10)	O6	Li1	O3	99.86(9)
C8	C9	C10	120.35(11)	N4	C11	C5	121.59(11)
O2	C10	C6	122.01(10)	O1	Li1	O5	102.05(9)
C11	N4	C3	120.50(10)	O1[1]	Li1	O5	153.95(11)
C7	N2	C8	120.84(10)	O1	Li1	O1[1]	86.43(8)
C7	C6	C10	121.03(11)	O1[1]	Li1	O3	100.79(9)
C11	C5	C1	120.40(10)	O1	Li1	O3	139.90(11)
N4	C3	C2	121.07(11)	O2	C10	C9	122.20(10)
			Mg-4HP				
O6	Mg1	O1	93.29(11)	O14	N3	O13	120.3(4)
O6	Mg1	O4	86.46(11)	O14	N3	O12	120.8(4)
O6	Mg1	O5	92.28(12)	C5	N1	C1	120.6(4)
O6	Mg1	O2	88.23(12)	C8	N2	C9	120.1(4)
O1	Mg1	O4	179.73(13)	O8	C6	C10	122.1(3)
O3	Mg1	O6	177.94(14)	O8	C6	C7	121.9(3)
O3	Mg1	O1	88.72(12)	C10	C6	C7	115.9(4)
O3	Mg1	O4	91.54(12)	O7	C3	C2	122.3(3)
O3	Mg1	O5	88.18(12)	O7	C3	C4	122.7(3)
O3	Mg1	O2	91.31(12)	C2	C3	C4	115.0(3)
O5	Mg1	O1	90.59(12)	C1	C2	C3	121.1(4)
O5	Mg1	O4	89.32(13)	C9	C10	C6	120.0(4)
O5	Mg1	O2	179.49(14)	N1	C1	C2	121.2(4)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O2	Mg1	O1	89.38(13)	C8	C7	C6	120.7(4)
O2	Mg1	O4	90.71(13)	C5	C4	C3	120.9(4)
O10	N4	O9	119.4(3)	N1	C5	C4	121.2(4)
O11	N4	O9	119.7(4)	N2	C9	C10	122.0(4)
O11	N4	O10	120.9(4)	N2	C8	C7	121.2(4)
O12	N3	O13	118.9(3)				

Table S5. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **Li-4HP**, **Li-4HP2**, and **Mg-4HP**.

Atom	*x*	*y*	*z*	$U_{(eq)}$
		Li-4HP		
H2A	7026.9	6986.59	5940.21	50
H2B	8425.21	7048.1	7231.4	50
H1	5450.61	6172.46	8160.72	39
H5	9152.96	4333.91	1071.01	35
H4	7460.85	4738.94	8585.31	41
H2	6623.46	6952.82	2586.91	35
H3	5008.96	7302.54	49.21	40
		Li-4HP2		
H6A	9537.12	1044.24	1296.02	39
H6B	10264.22	1442.95	9859.22	39
H4	1345.57	7682.56	2040.91	25
H2A	2877.4	88362.9	4596.34	28
H6	5758.26	1215.29	2511	24
H5	6181.32	8201.62	9688.3	23
H3	2608.06	5220.76	2806.65	25
H11	3008.67	9168.51	517.67	25
H9	8277.93	6646.81	3523.05	25
H8	5407.3	6328.43	4602.25	28
H7	2950.46	777.53	3627.81	27
H2	5769.4	4145.74	2069	22
		Mg-4HP		
H6A	4598.43	3957.01	5958.13	57
H6B	5159	3778.36	6029.46	57
H1A	4760.19	4962.9	6907.34	52
H1B	5101.31	6410.23	7208.17	52
H3A	4897.35	973.77	6728.25	60
H3B	5413.16	1076.07	6652.08	60
H4A	5220.17	956.86	5610.4	54
H4B	4924.09	8279.29	5321.68	54
H5A	6007.99	5609.6	6682.33	59
H5B	6125.76	7655.16	6675.41	59
H2A	3886.37	7172.57	5837	63
H2B	3998.82	9226.72	5848.44	63
H1	7530.38	4267.92	5622.89	52
H2	2457.43	721.63	6861.81	59
H2C	6014.33	6056.19	5581.47	46
H10	3981.05	8806.88	6965.08	55

Atom	*x*	*y*	*z*	$U_{(eq)}$
H1C	6933.89	6815.87	5675.73	53
H7	3631.92	4918.04	7057.81	56
H4	6358.51	26.34	5340.01	51
H5	7274.04	956.17	5454.69	58
H9	3055.98	8812.87	6876.63	66
H8	2714.61	4051.15	6954.44	64

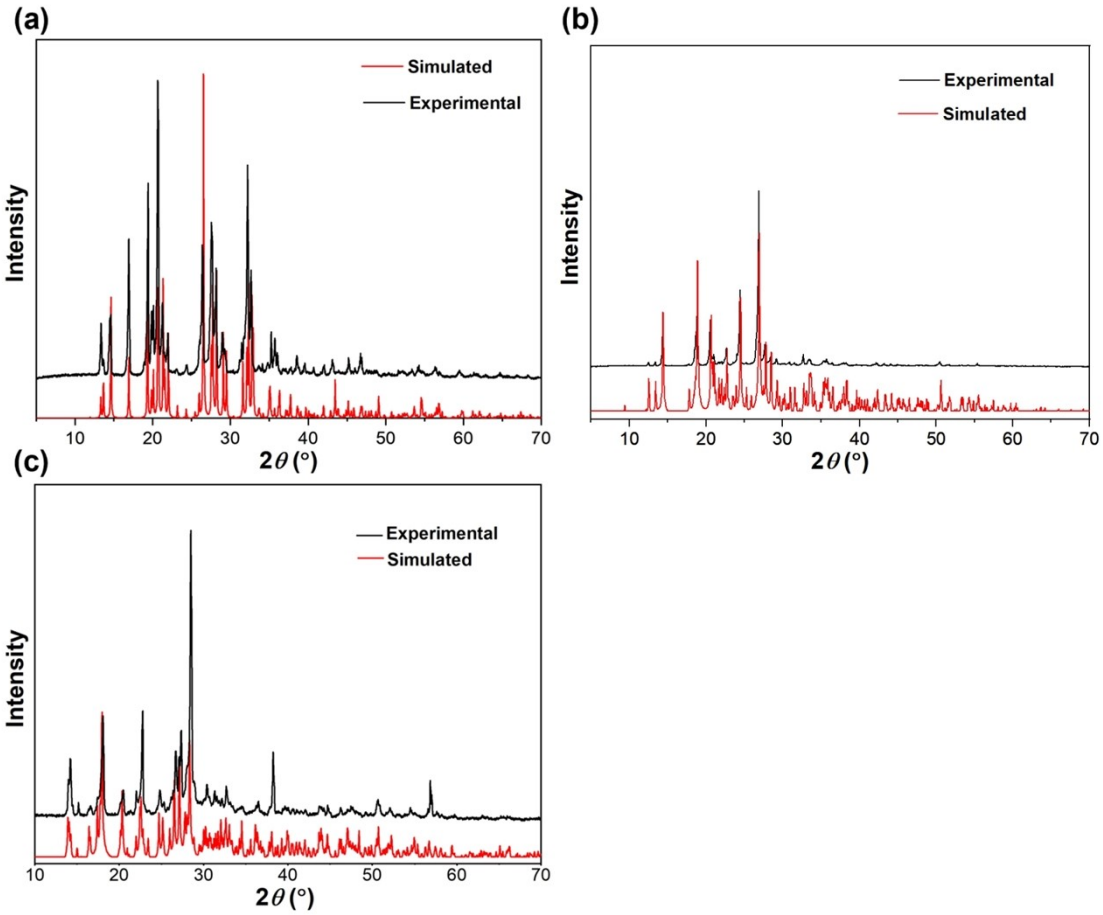


Fig. S1 Experimental and simulated PXRD patterns of (a) **Li-4HP**, (b) **Li-4HP2**, and (c) **Mg-4HP**.

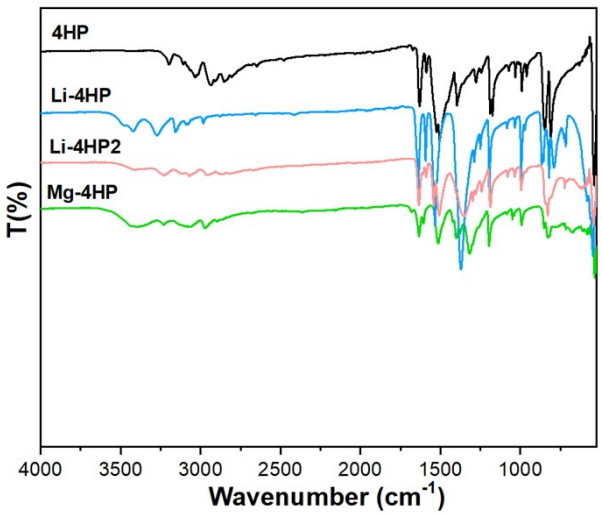


Fig. S2 IR spectra for **4HP**, **Li-4HP**, **Li-4HP2**, and **Mg-4HP**.

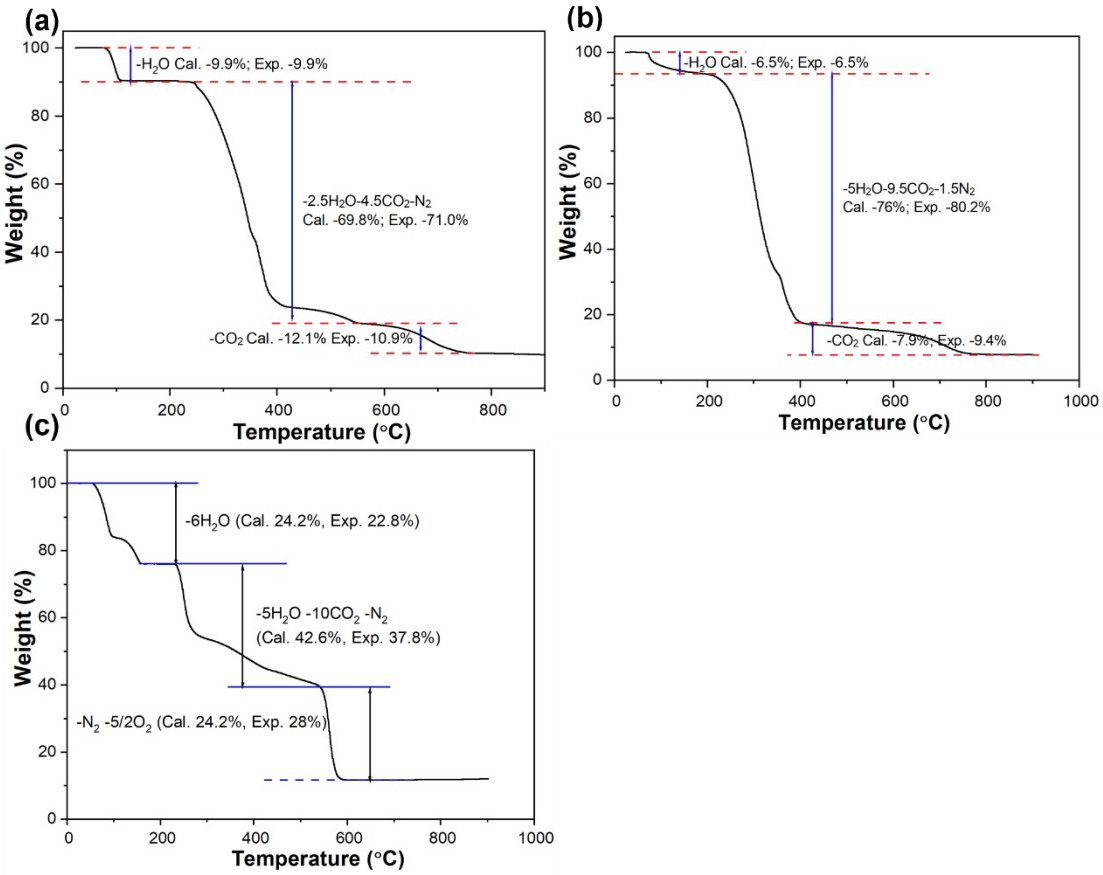


Fig. S3 TGA diagrams of (a) **Li-4HP**, (b) **Li-4HP2**, and (c) **Mg-4HP**.

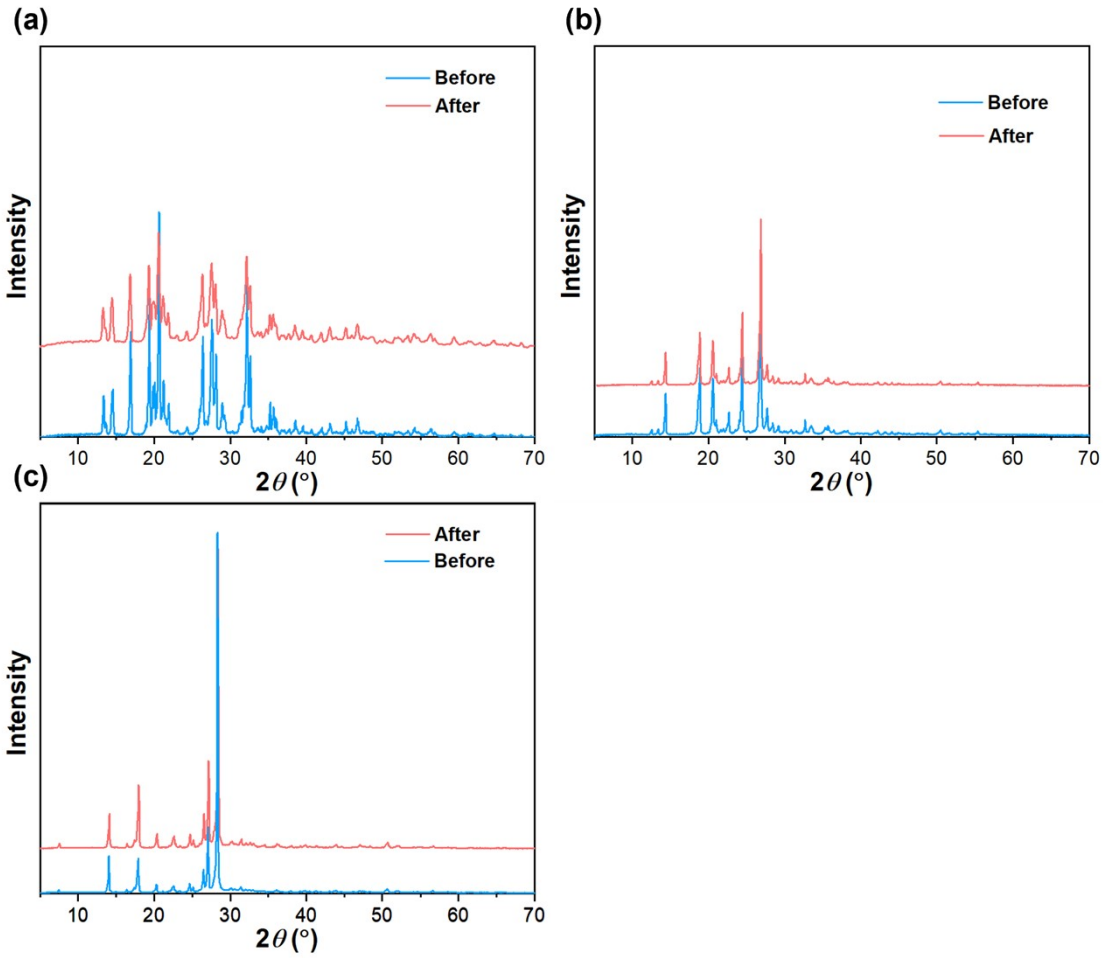


Fig. S4 PXRD patterns of (a) **Li-4HP**, (b) **Li-4HP2**, and (c) **Mg-4HP** before (Blue) and after (Red) exposure to air.

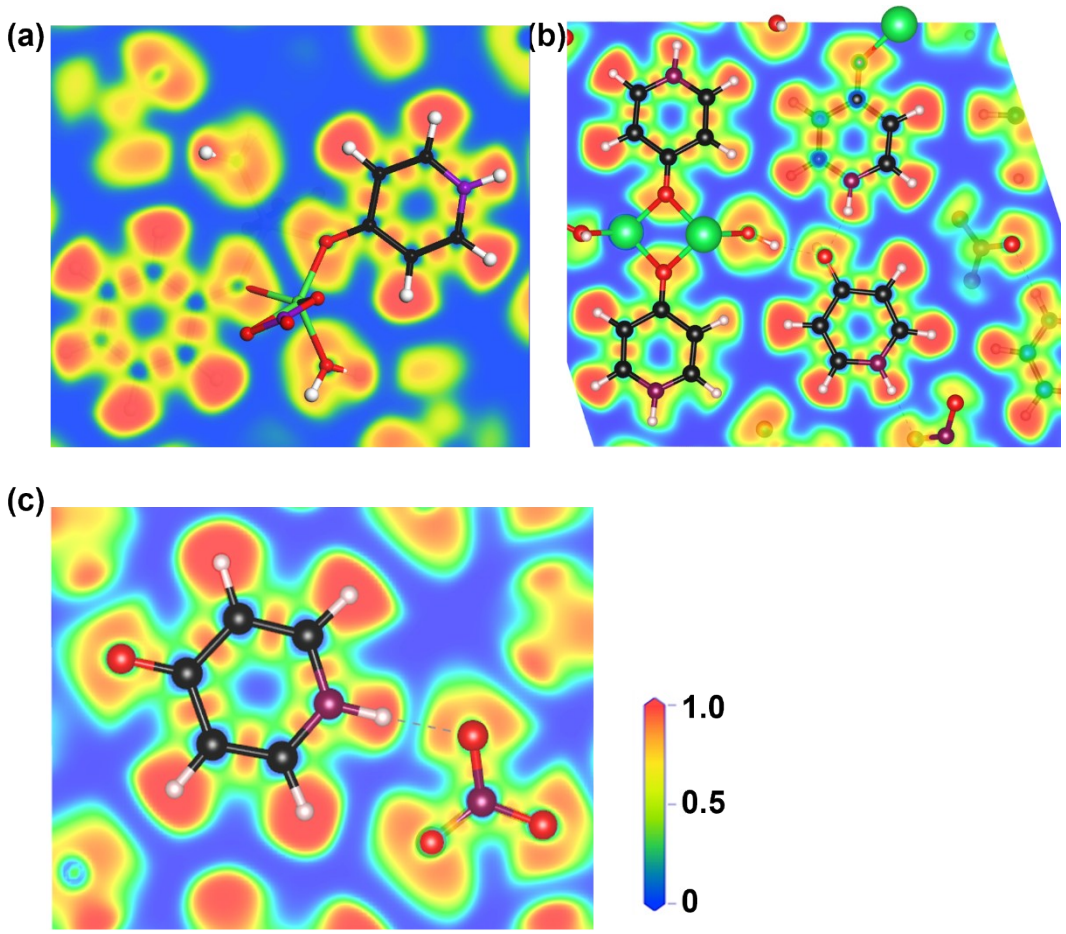


Fig. S5 ELF diagrams of (a) **Li-4HP**, (b) **Li-4HP2**, and (c) **Mg-4HP**.

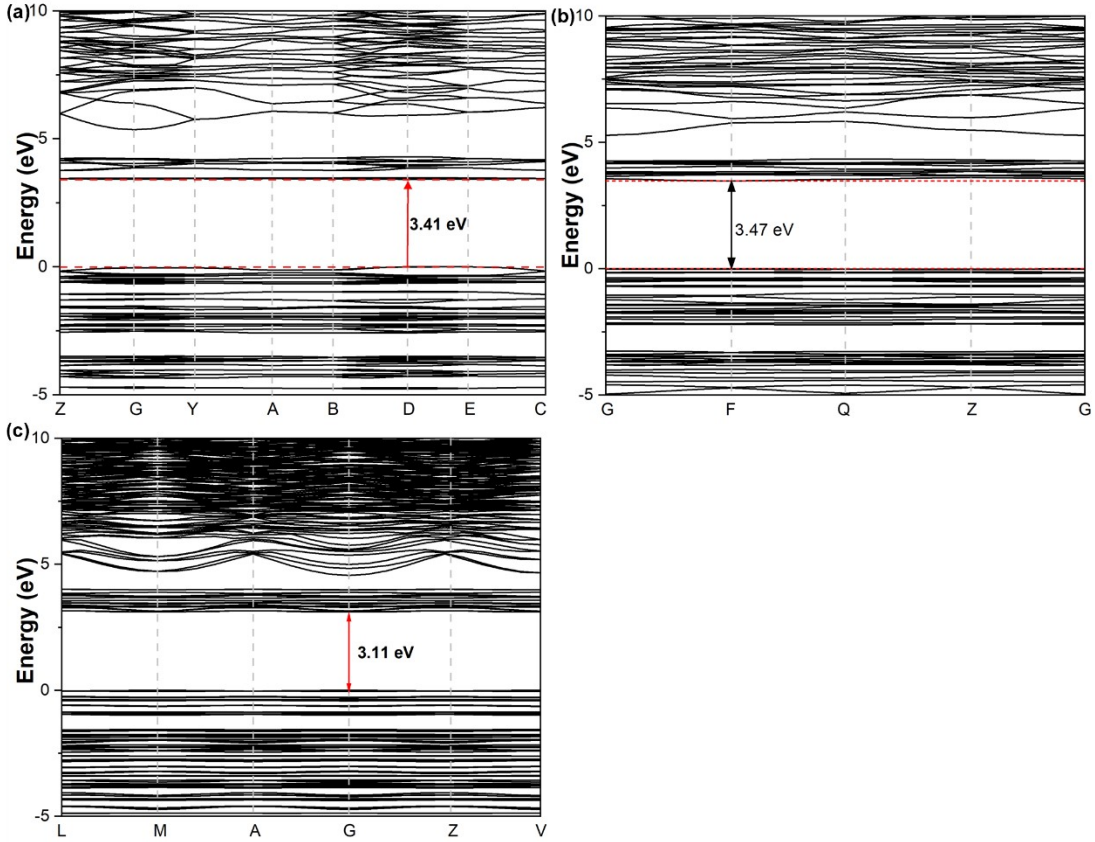


Fig. S6 Band structures of (a) **Li-4HP**, (b) **Li-4HP2**, and (c) **Mg-4HP.**

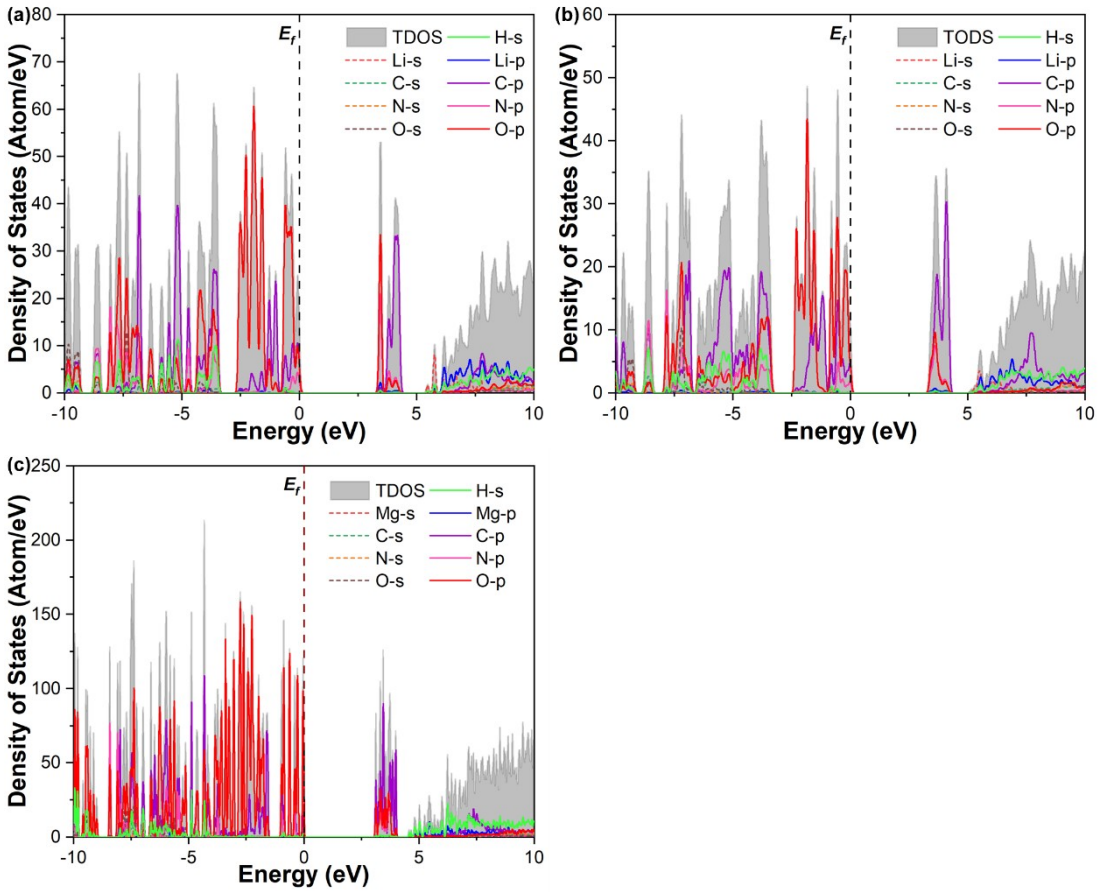


Fig. S7 Total and partial DOS for (a) **Li-4HP**, (b) **Li-4HP2**, and (c) **Mg-4HP**.

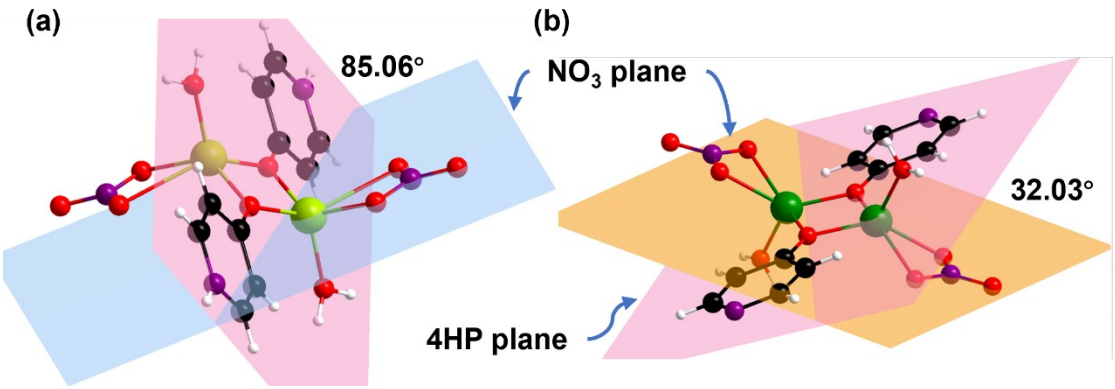
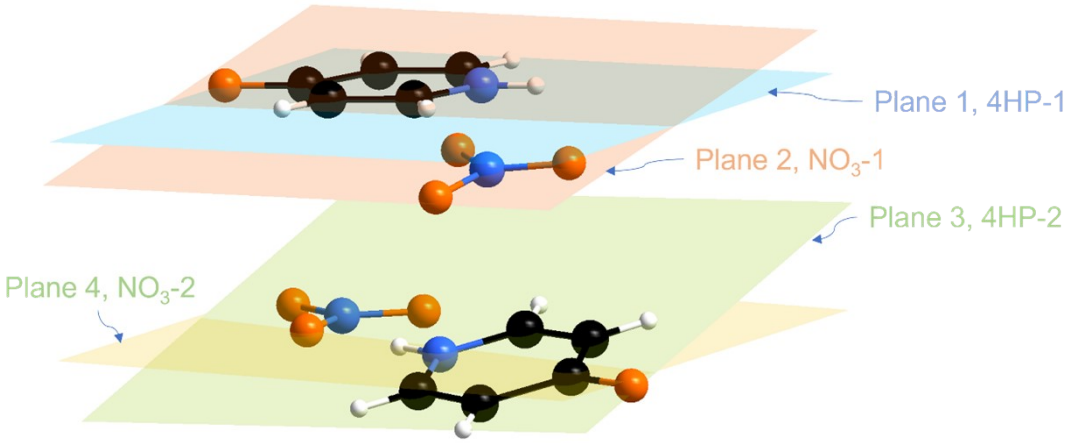


Fig. S8 Dihedral angles between **4HP** and NO_3 among the $[LiNO_3 \cdot H_2O \cdot \mathbf{4HP}]_2$ dimers in (a) **Li-4HP** and (b) **Li-4HP2**.



	4HP-1	NO_3-1	4HP-1	NO_3-1
4HP-1		**9.51**	**14.42**	**1.45**
NO_3-1	**9.51**		**5.02**	**9.88**
4HP-2	**14.42**	**5.02**		**14.88**
NO_3-2	**1.45**	**9.88**	**14.88**	

Fig. S9 Dihedral angles between the coplanar groups in **Mg-4HP**.

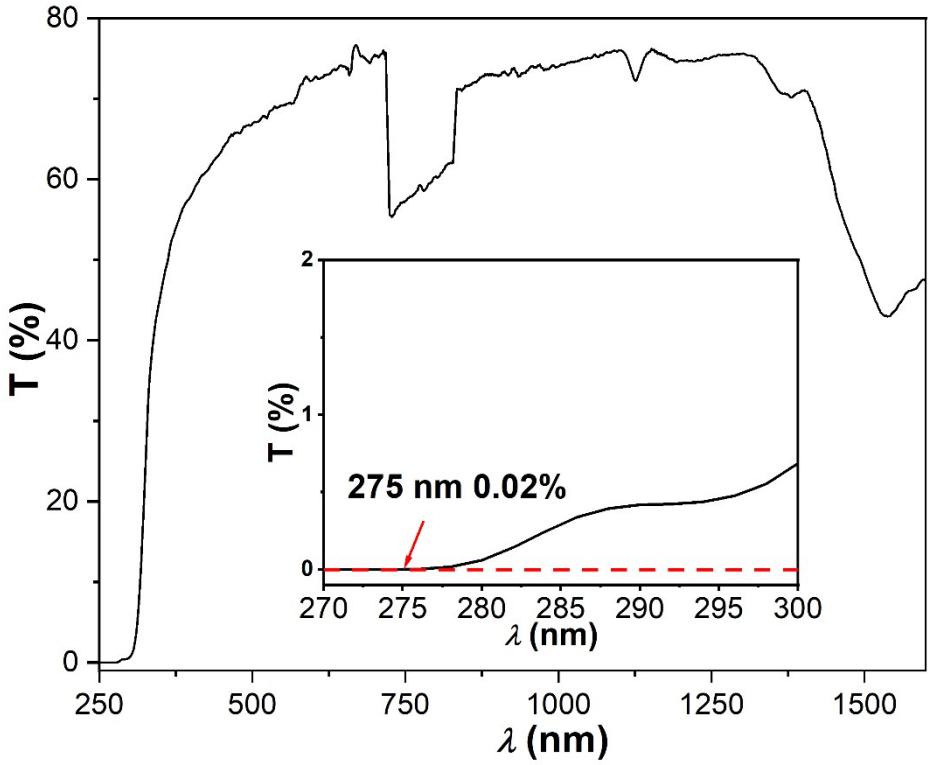


Fig. S10 UV-vis-NIR transmittance spectrum for **Mg-4HP**.

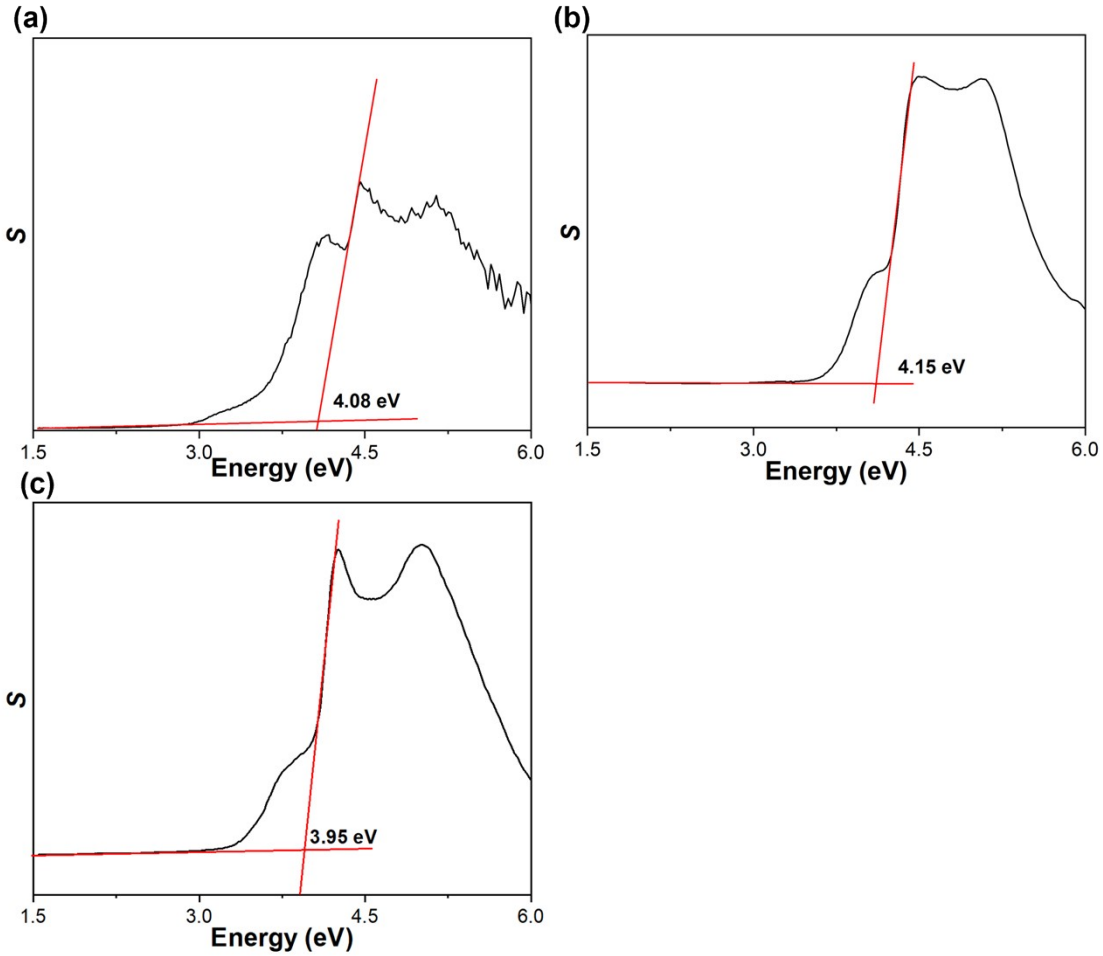


Fig. S11 Experimental bandgaps for (a) **Li-4HP**, (b) **Li-4HP2**, and (c) **4HP**.

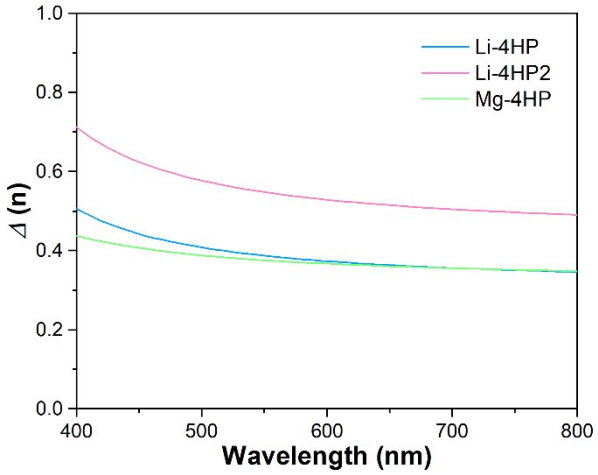


Fig. S12 Calculated birefringence of **Li-4HP**, **Li-4HP2**, and **Mg-4HP**.

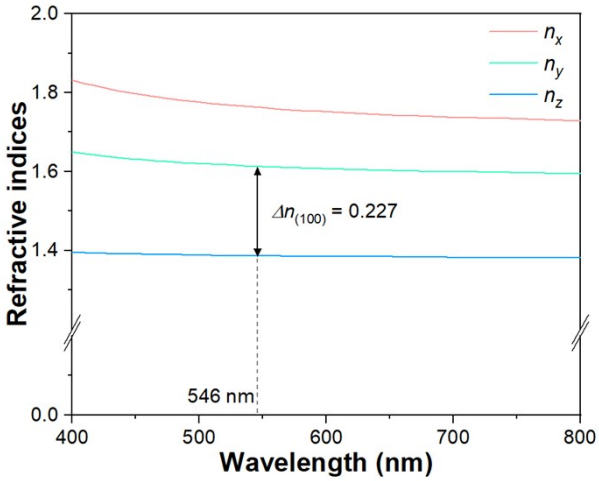


Fig. S13 Calculated refractive indices and birefringence on (100) crystal plane of **Mg-4HP**.

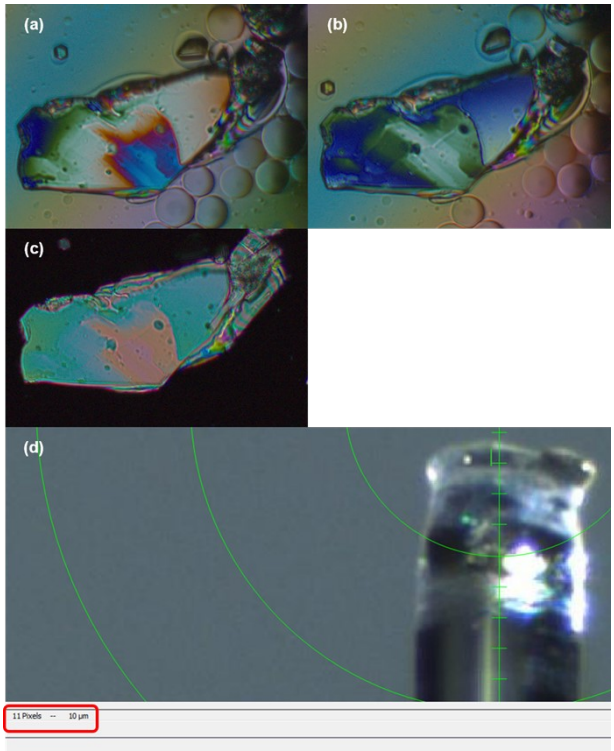


Fig. S14 (a-c) a **Li-4HP** crystal observed under cross-polarized light achieving complete extinction under a polarizing microscope and (d) thickness of a **Li-4HP** crystal.

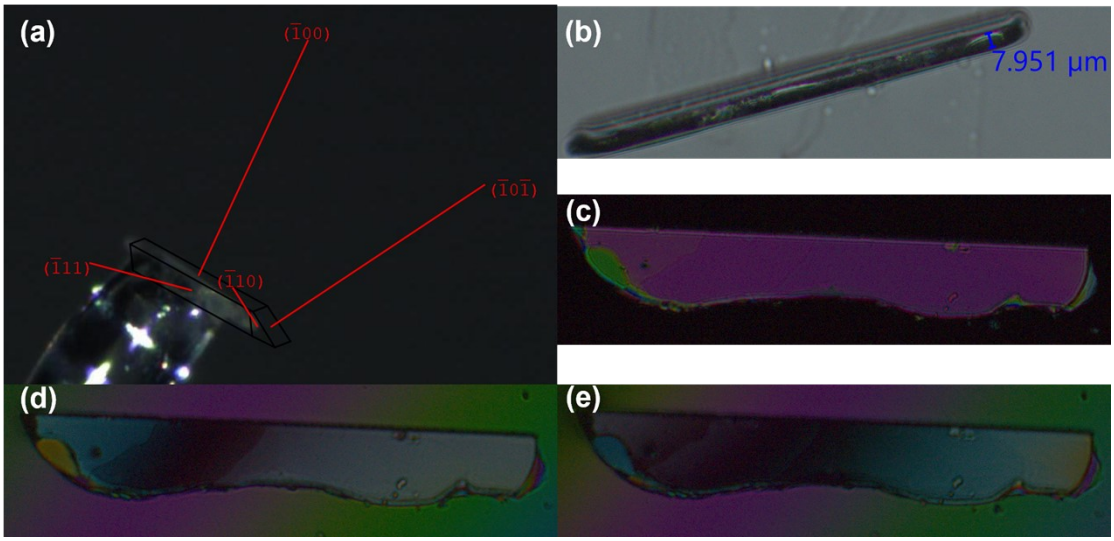


Fig. S15 (a) Crystal orientation observed via the single-crystal XRD; (b) Thickness of a **Mg-4HP** crystal and (c-e) a **Mg-4HP** crystal observed under cross-polarized light achieving complete extinction under a polarizing microscope.

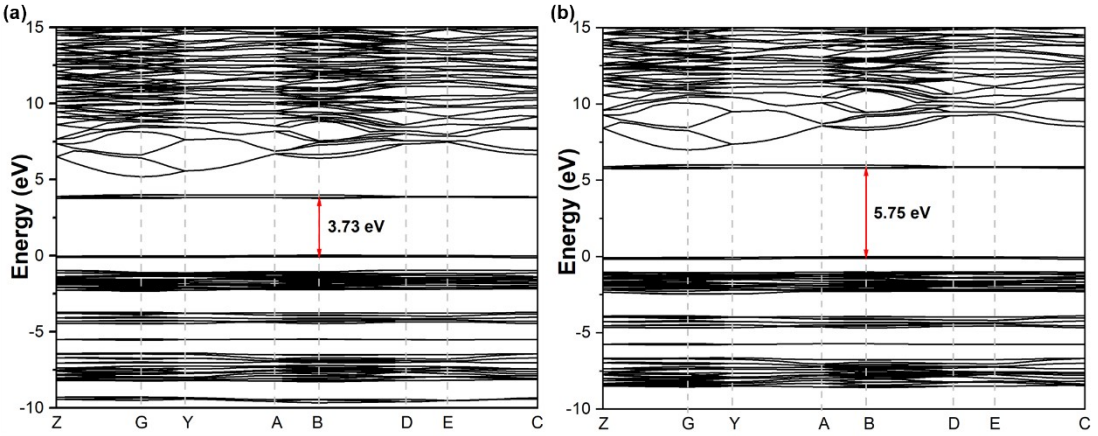


Fig. S16 Band structures of $Mg(NO_3)_2{\cdot}6H_2O$ depicted by (a) GGA functional and (b) HSE06 functional.

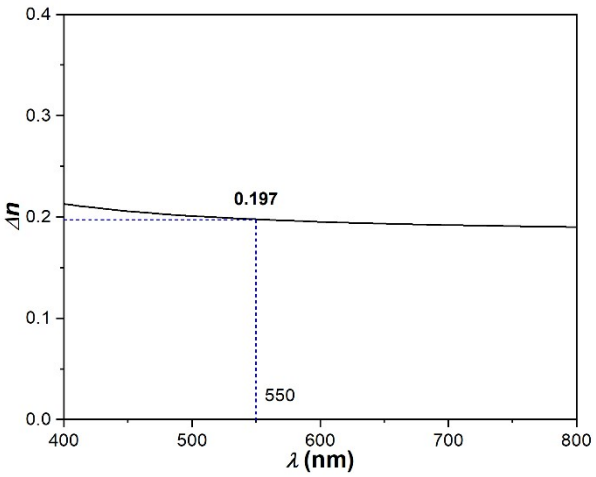


Fig. S17 Calculated birefringence of $Mg(NO_3)_2{\cdot}6H_2O$.

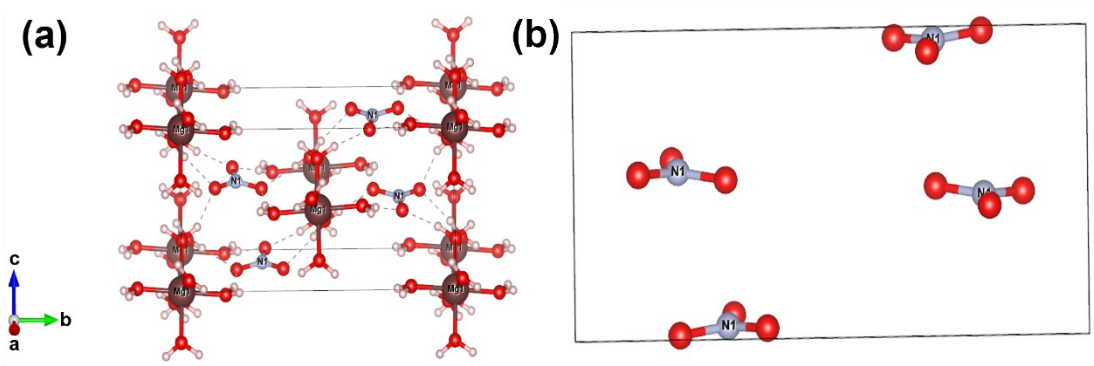
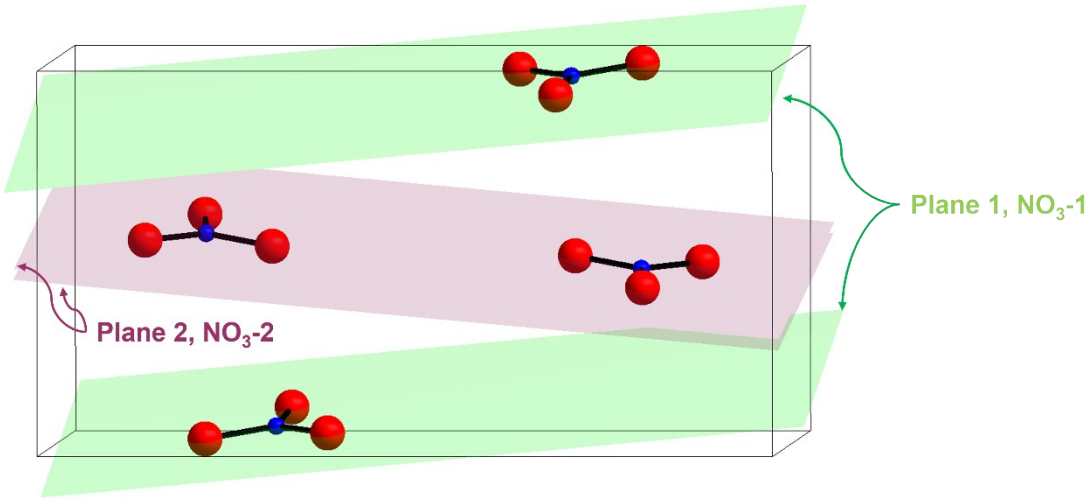


Fig. S18 Ball-and-stick representations of (a) $Mg(NO_3)_2 \cdot 6H_2O$ and (b) NO_3 in the lattice viewed along the *a*-axis.



	NO_3-1
NO_3-2	**10.37°**

Fig. S19 Dihedral angles between the NO_3 groups in $Mg(NO_3)_2 \cdot 6H_2O$.