Supplementary Information (SI) for Chemical Science.
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Electronic Supplementary Information (ESI) for

Synergistic engineering of ultraviolet metal-free crystals with exceptional birefringence via pyridine-derived dimers

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Table S1. Crystallographic data for **1** and **2**.

Empirical formula	$C_{15}H_{15}N_3O_5S$ (**1**)	$C_{10}H_{11}N_3O_3S$ (**2**)
Formula weight	349.36	253.28
Temperature/K	303.00	303.00
CCDC number	2393748	2393642
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pbcn*
a/Å	17.5972(5)	7.2257(4)
b/Å	7.0455(2)	13.4248(8)
c/Å	12.8268(3)	24.3820(14)
α/°	90	90
β/°	90.8810(10)	90
γ/°	90	90
Volume/Å^3	1590.09(7)	2365.1(2)
Z	4	8
ρ_{calc} g/cm^3	1.459	1.423
μ/mm^{-1}	0.235	0.274
F(000)	728.0	1056
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2ϑ range/°	4.63 to 56.61	6.07 to 56.766
Index ranges	-23 ≤ *h* ≤ 23, -9 ≤ *k* ≤ 9, -17 ≤ *l* ≤ 17	-9 ≤ *h* ≤ 9, -17 ≤ *k* ≤ 17, -32 ≤ *l* ≤ 32
Reflections collected	35676	27477
Independent reflections	3957 [R_{int} = 0.0581, R_{sigma} = 0.0305]	2963 [R_{int} = 0.0786, R_{sigma} = 0.0460]
Data/restraints/parameters	3957/0/217	2963/0/198
Goodness-of-fit on F^2	1.136	1.209
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0524, wR_2 = 0.1062	R_1 = 0.0779, wR_2 = 0.1283
Final *R* indexes [all data]	R_1 = 0.0762, wR_2 = 0.1195	R_1 = 0.1243, wR_2 = 0.1474
Largest diff. peak/hole / e Å^{-3}	0.22/-0.33	0.23/-0.31

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

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	$U_{(eq)}$
S1	3484.7(3)	1218.5(8)	4363.5(4)	38.54(15)
O5	3425.2(9)	1404(3)	5488.2(12)	54.2(4)
O3	3762.0(9)	-620(2)	4046.8(15)	57.4(5)
O2	9337.9(8)	3264(3)	3598.3(13)	57.5(5)
O4	2795.5(8)	1786(3)	3822.0(14)	58.5(5)
N3	5494.3(9)	3831(3)	4053.9(14)	40.3(4)
O1	9645.3(9)	3285(3)	1749.6(13)	68.3(6)
N2	7085.5(10)	3431(3)	4204.6(15)	46.5(5)
N1	11884.0(10)	3354(3)	1067.4(16)	48.6(5)
C14	4190.7(10)	2870(3)	3983.2(15)	33.5(4)
C15	4940.2(11)	2630(3)	4306.1(16)	36.7(4)
C11	5308.7(13)	5330(3)	3474.4(17)	45.8(5)
C13	4012.3(13)	4426(4)	3372.5(18)	47.5(5)
C6	8617.5(11)	3337(3)	3774.6(17)	40.8(5)
C8	7314.3(12)	3632(4)	3218.5(19)	47.9(5)
C7	8064.5(12)	3598(3)	2978.6(18)	44.8(5)
C10	8353.0(12)	3155(3)	4800.1(17)	45.0(5)
C4	10930.9(12)	3438(4)	2326.7(18)	51.3(6)
C2	10610.8(13)	3183(4)	508.6(19)	52.2(6)
C9	7593.1(13)	3199(4)	4985.7(18)	48.6(6)
C3	10365.5(12)	3299(4)	1543.8(18)	48.0(6)
C5	11677.8(13)	3447(4)	2062(2)	53.2(6)
C12	4579.7(14)	5679(4)	3119.2(19)	54.4(6)
C1	11361.4(13)	3230(4)	298(2)	51.4(6)

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of non-hydrogen atoms for compound **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	$U_{(eq)}$
S1	8764.5(13)	5435.5(6)	6033.0(3)	44.9(2)
O3	8662(4)	4360.0(16)	5992.4(10)	55.1(7)
O1	10584(4)	5818(2)	5902.7(10)	67.5(8)
O2	8032(5)	5805(2)	6548.1(9)	71.6(9)
N3	6800(4)	6384(2)	4584.7(11)	50.0(7)
N1	7627(5)	7094(3)	1807.5(12)	57.8(9)
N2	7392(5)	6584(3)	3456.5(13)	57.8(9)
C9	7257(5)	5898(2)	5517.4(12)	39.3(7)
C10	7899(5)	6075(3)	4993.2(13)	43.0(8)
C3	7531(5)	6924(3)	2347.5(12)	44.3(8)
C4	7673(6)	5956(3)	2561.5(15)	52.6(9)
C8	5395(6)	6041(3)	5623.4(16)	54.2(10)
C2	7269(6)	7704(3)	2720.9(14)	52.3(9)
C5	7615(6)	5812(3)	3110.5(16)	59.0(10)
C6	5018(6)	6525(3)	4698.2(17)	57.1(10)
C1	7200(6)	7507(3)	3266.9(15)	57.9(10)
C7	4262(6)	6361(3)	5207.0(19)	62.9(11)

Table S4. Bond lengths for compound **1** and **2**.

Bond	Length/Å	Bond	Length/Å
	1		
S1-O5	1.4539(16)	C14-C15	1.387(3)
S1-O3	1.4447(17)	C14-C13	1.381(3)
S1-O4	1.4448(16)	C11-C12	1.377(3)
S1-C14	1.776(2)	C13-C12	1.376(3)
O2-C6	1.292(2)	C6-C7	1.412(3)
N3-C15	1.335(3)	C6-C10	1.408(3)
N3-C11	1.330(3)	C8-C7	1.360(3)
O1-C3	1.298(3)	C10-C9	1.362(3)
N2-C8	1.341(3)	C4-C3	1.406(3)
N2-C9	1.342(3)	C4-C5	1.362(3)
N1-C5	1.334(3)	C2-C3	1.405(3)
N1-C1	1.341(3)	C2-C1	1.353(3)
	2		
S1-O3	1.449(2)	C9-C10	1.381(4)
S1-O1	1.447(3)	C9-C8	1.383(5)
S1-O2	1.450(2)	C3-C4	1.405(5)
S1-C9	1.776(3)	C3-C2	1.400(5)
N3-C10	1.340(4)	C4-C5	1.353(5)
N3-C6	1.330(5)	C8-C7	1.373(6)
N1-C3	1.338(4)	C2-C1	1.358(5)
N2-C5	1.347(5)	C6-C7	1.374(6)
N2-C1	1.329(5)		

Table S5. Bond angles for compound **1** and **2**.

Bond	Angle/°	Bond	Angle/°
		1	
O5-S1-C14	105.96(9)	O2-C6-C7	123.1(2)
O3-S1-O5	112.92(11)	O2-C6-C10	119.9(2)
O3-S1-O4	113.43(11)	C10-C6-C7	116.97(19)
O3-S1-C14	105.64(9)	N2-C8-C7	121.2(2)
O4-S1-O5	112.30(10)	C8-C7-C6	119.9(2)
O4-S1-C14	105.80(10)	C9-C10-C6	120.1(2)
C11-N3-C15	117.73(18)	C5-C4-C3	119.8(2)
C8-N2-C9	120.74(18)	C1-C2-C3	120.2(2)
C5-N1-C1	120.90(19)	N2-C9-C10	121.1(2)
C15-C14-S1	120.26(16)	O1-C3-C4	122.5(2)
C13-C14-S1	121.47(16)	O1-C3-C2	120.4(2)
C13-C14-C15	118.27(19)	C2-C3-C4	117.0(2)
N3-C15-C14	123.03(19)	N1-C5-C4	121.0(2)
N3-C11-C12	123.1(2)	C13-C12-C11	118.9(2)
C12-C13-C14	119.0(2)	N1-C1-C2	121.0(2)
		2	
O3-S1-O2	112.41(16)	N3-C10-C9	122.9(3)
O3-S1-C9	105.59(15)	N1-C3-C4	121.3(3)
O1-S1-O3	112.66(17)	N1-C3-C2	121.3(3)
O1-S1-O2	113.59(18)	C2-C3-C4	117.4(3)
O1-S1-C9	106.13(15)	C5-C4-C3	119.8(4)
O2-S1-C9	105.65(16)	C7-C8-C9	119.0(4)
C6-N3-C10	117.6(3)	C1-C2-C3	119.8(4)
C1-N2-C5	120.8(3)	N2-C5-C4	120.9(4)
C10-C9-S1	120.6(3)	N3-C6-C7	123.4(4)
C10-C9-C8	118.4(3)	N2-C1-C2	121.2(4)
C8-C9-S1	120.9(3)	C8-C7-C6	118.7(4)

Table S6. Hydrogen bonds for compound **1** and **2**.

D-H···A	d(D-A)/Å	D-H···A/°
	1	
O2-H2···O1	2.440(2)	166.5
N2-H2A···N3	2.818(2)	157.0
N1-H1···O5[1]	2.828(2)	175.1
	2	
N1-H1A···O3[2]	2.884(4)	168(4)
N1-H1B···O2[3]	2.930(5)	167(3)
N2-H2···N3	2.797(4)	167(4)

Symmetry codes: [1]1+*X*,1/2-*Y*,-1/2+*Z*; [2]+*X*,1-*Y*,-1/2+*Z*; [3]3/2-*X*,3/2-*Y*,-1/2+*Z*

Table S7. Comparison of experimental birefringence among metal-free compounds containing single six-membered rings in short-wave ultraviolet region.

Number	Compound	UV cutoff edge	Birefringence	Reference
1	[(4-HP)(4-H_2P)][3-pySO_3]	279 nm[b]	0.443 @546 nm	This work
2	($C_6H_6NO_2$)Cl	262 nm[b]	0.363 @550 nm	1
3	($C_7H_4NO_4$)(IO_3)	269 nm[b]	0.350 @546 nm	2
4	($C_3H_7N_6$)F·H_2O	220 nm[b]	0.337@550 nm	3
5	($C_3N_6H_7$)BF_4·H_2O	244 nm[a]	0.310 @546 nm	4
6	β-($C_3H_7N_6$)$_2Cl_2$·H_2O	230 nm[b]	0.299 @550 nm	3
7	(3CP)(H_2PO_4)	270 nm[b]	0.284 @546 nm	5
8	2($C_3H_7N_6$)·2Cl·H_2O	245 nm[b]	0.248 @546 nm	6
9	$C_3N_6H_7SO_3NH_2$	206 nm[b]	0.240 @546 nm	7
10	(C_5H_6NO)(CH_3SO_3)	252 nm[b]	0.216 @546 nm	8
11	($C_3N_6H_7$)SO_3CH_3·H_2O	233 nm[b]	0.200 @546 nm	4
12	(3AP)(H_2PO_4)	265 nm[b]	0.196 @546 nm	5
13	$BC_2N_5H_6(OH)_2$·H_2O	240 nm[a]	0.181 @546 nm	9
14	(C_5H_6N)$_2B_2O$(HPO_4)$_2$	270 nm[b]	0.156 @546 nm	10
15	($C_3N_2H_5$)$B_3O_3F_2(OH)_2$	214 nm[a]	0.150 @546 nm	11

[a]Transmittance spectrum; [b]Diffuse reflectance spectrum.

Table S8. Comparison of experimental birefringence among UV sulfate derivatives that incorporate an additional birefringence-active group (BAG).

Number	Compound	UV cutoff edge	Birefringence	Reference
1	[(4-HP)(4-H_2P)][3-pySO_3]	279 nm[b]	0.443 @546 nm	This work
2	$C_3N_6H_7SO_3NH_2$	206 nm[b]	0.240 @546 nm	7
3	(C_5H_6NO)(CH_3SO_3)	252 nm[b]	0.216 @546 nm	8
4	Bi(SeO_3)(CH_3SO_3)	277 nm[b]	0.160 @546 nm	12
5	Bi(TeO_3)(CH_3SO_3)	274 nm[b]	0.145 @546 nm	12
6	[$C(NH_2)_3$]S_3O_6	218 nm[b]	0.097 @546 nm	13
7	$KNO_3SO_3NH_3$	216 nm[b]	0.095 @546 nm	14
8	[$C(NH_2)_3$]$_2S_2O_8$	222 nm[b]	0.081 @546 nm	15
9	[$C(NH_2)_3$]$_2SO_3S$	254 nm[a]	0.073 @546 nm	16
10	$RbNO_3SO_3NH_3$	208 nm[b]	0.070 @546 nm	17
11	Sr(NO_3)(NH_2SO_3)·H_2O	290 nm[a]	0.067 @532 nm	18
12	$Na_{10}Zn(NO_3)_4(SO_3S)_4$	240 nm[b]	0.013 @550 nm	19

[a]Transmittance spectrum, [b]diffuse reflectance spectrum.

Table S9. Birefringence values for selected commercial birefringent crystals.

Number	Compound	Birefringence	Reference
1	TiO_2	0.305 @546 nm	20
2	YVO_4	0.225 @633 nm	21
3	$CaCO_3$	0.172 @589 nm	22
4	$LiNbO_3$	0.074 @546 nm	23

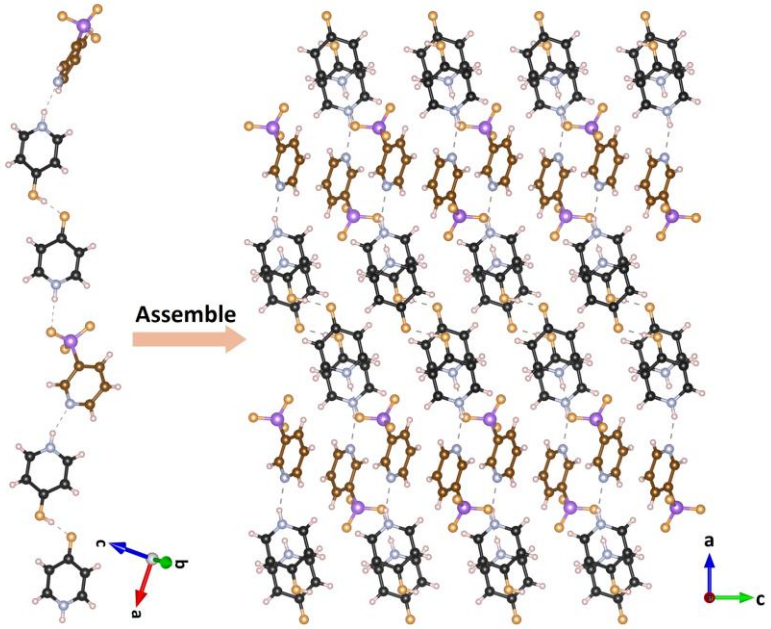

Fig. S1 One-dimensional (1D) $[(4\text{-HP})(4\text{-}H_2P)][3\text{-}pySO_3]_\infty$ chains in compound **1**.

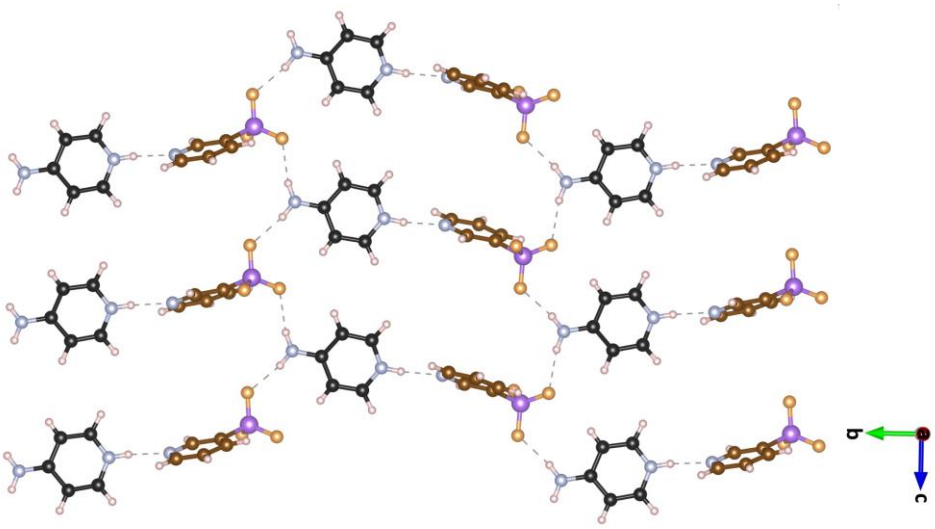

Fig. S2 The two-dimensional (2D) $[4\text{-}AP(3\text{-}pySO_3)]_\infty$ layers in compound **2**.

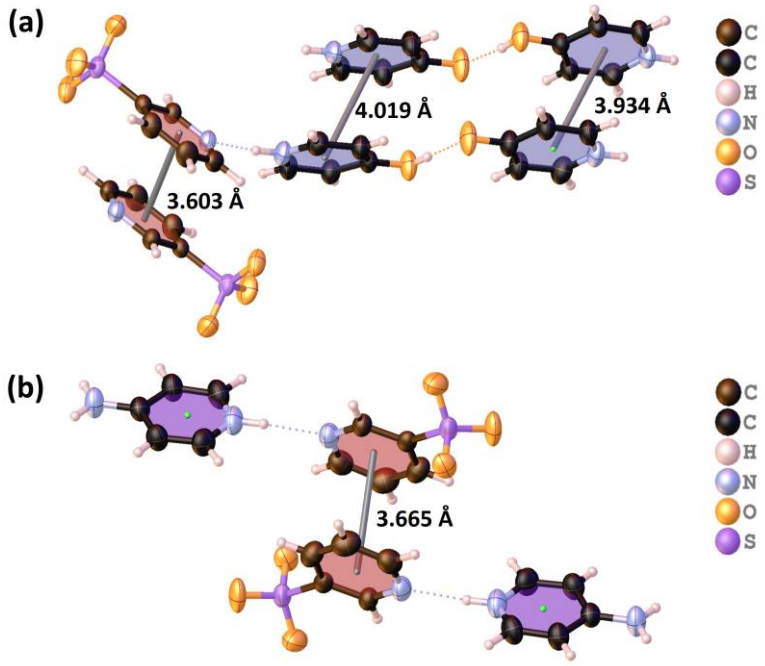

Fig. S3 π-π interactions in (a) compound **1** and (b) compound **2**.

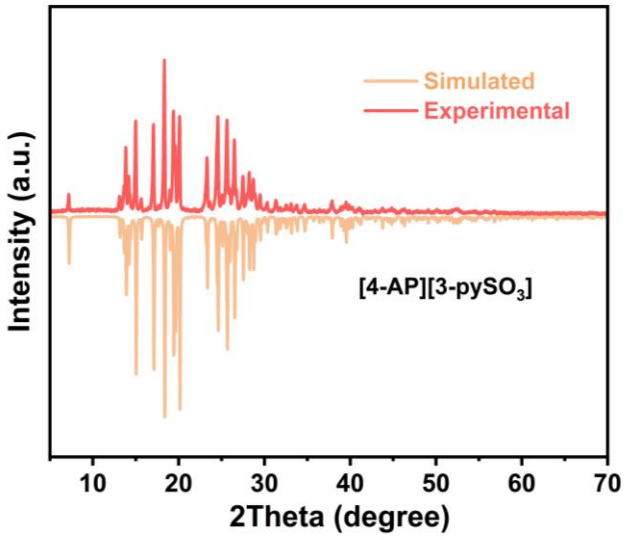

Fig. S4 Simulated and experimental PXRD patterns of compound **2**.

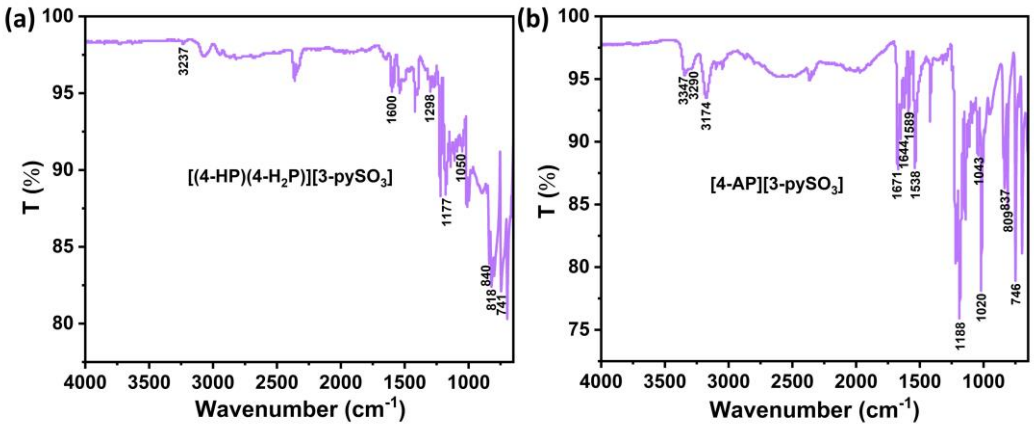

Fig. S5 IR spectra of (a) compound **1** and (b) compound **2**.

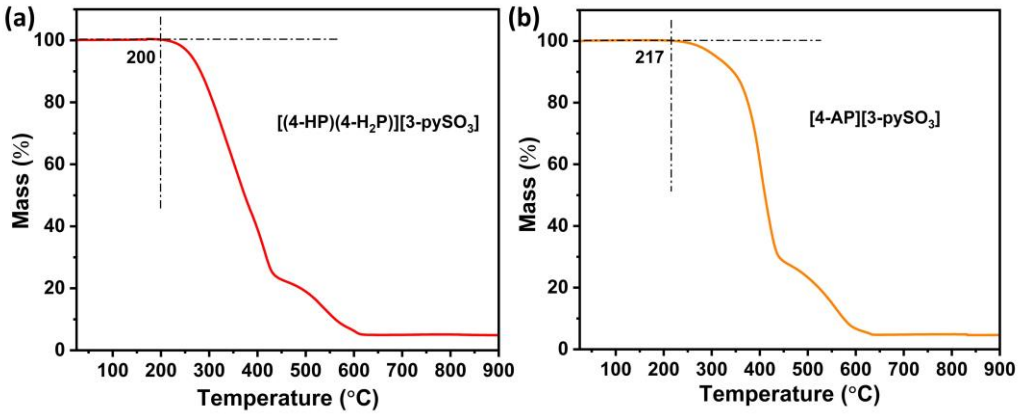

Fig. S6 TGA diagrams of (a) compound **1** and (b) compound **2**.

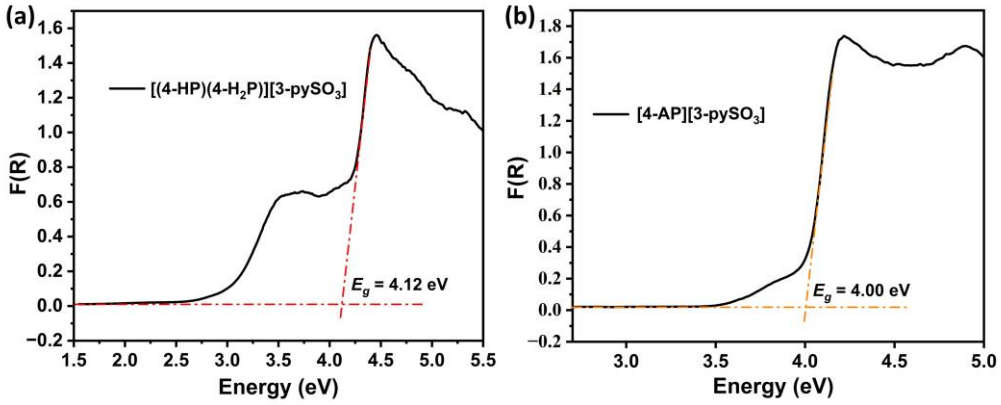

Fig. S7 Experimental band gaps for (a) compound **1** and (b) compound **2**.

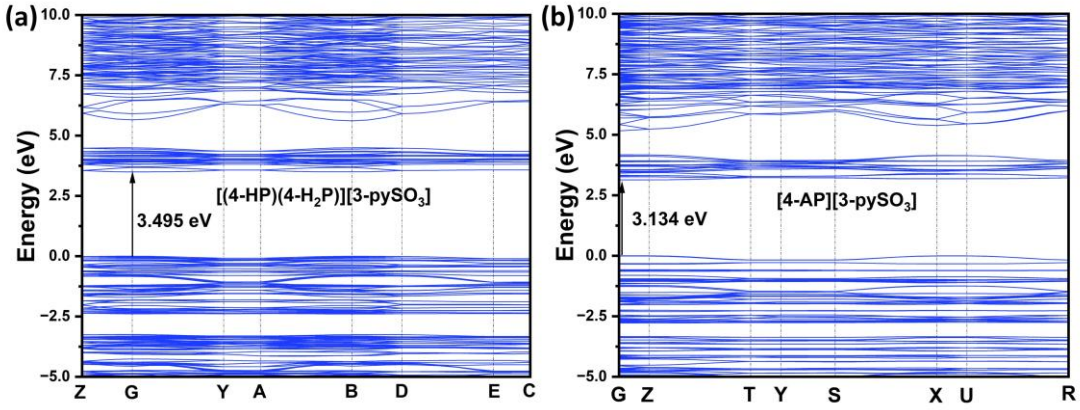

Fig. S8 Calculated band gaps for (a) compound **1** and (b) compound **2**.

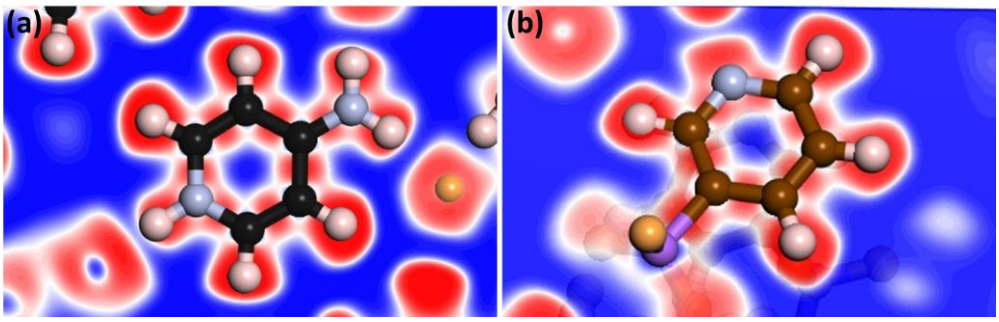

Fig. S9 ELF diagrams of (a) $[4\text{-AP}]^+$ and (b) $[3\text{-pySO}_3]^-$ groups in compound **2**.

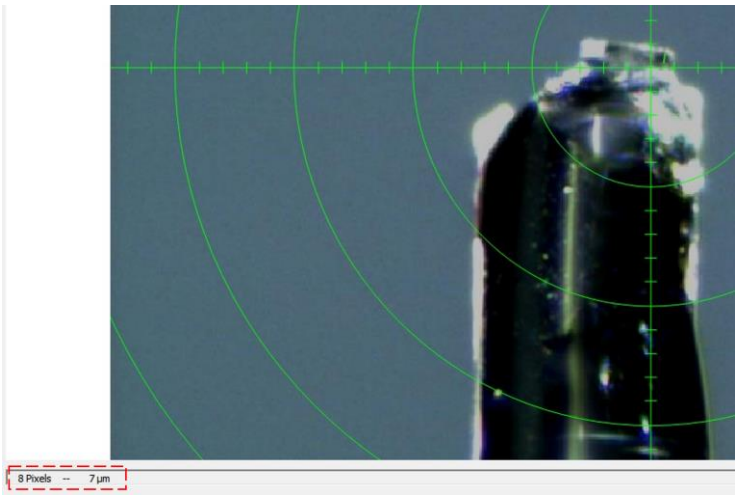

Fig. S10 Thickness of compound **1** crystal for birefringence measurement.

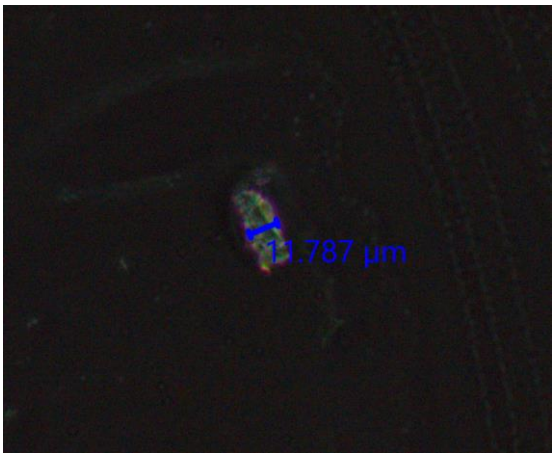

Fig. S11 Thickness of compound **2** crystal for birefringence measurement.

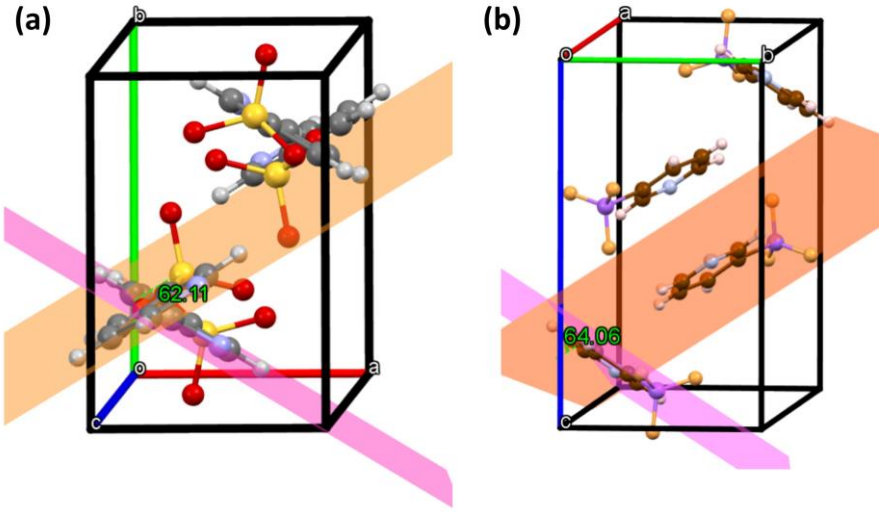

Fig. S12 Dihedral angle between $[3\text{-py}SO_3]^-$ groups in (a) $Li(3\text{-py}SO_3)\cdot H_2O$ and (b) compound **1**.

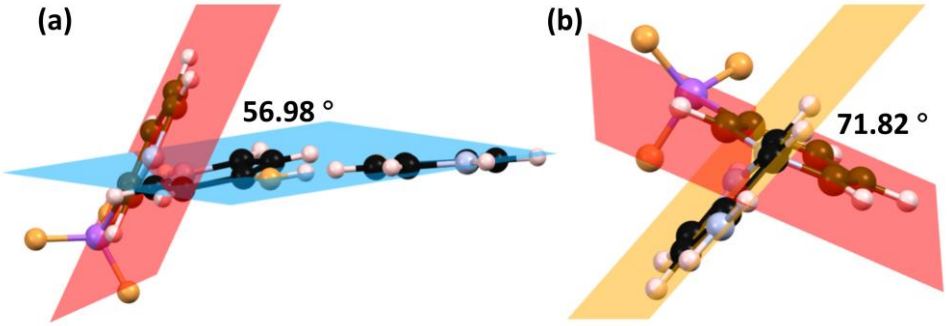

Fig. S13 (a) Dihedral angle between $[3\text{-py}SO_3]^-$ and $[4\text{-HP}/4\text{-}H_2P]^+$ in compound **1**; (b) Dihedral angle between $[3\text{-py}SO_3]^-$ and $[4\text{-AP}]^+$ in compound **2**.

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