Supplementary Information

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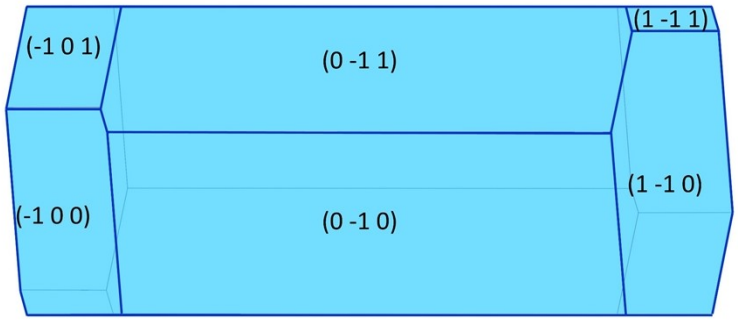

Fig. S1 The theoretical morphology of $(C_3N_6H_7)BF_4 \cdot H_2O$.

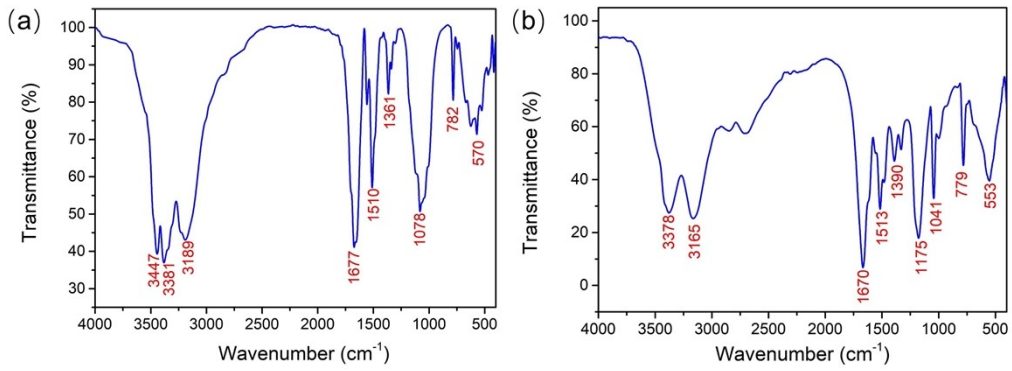

Fig. S2 Infrared spectra for (a) $(C_3N_6H_7)BF_4 \cdot H_2O$ and (b) $(C_3N_6H_7)SO_3CH_3 \cdot H_2O$.

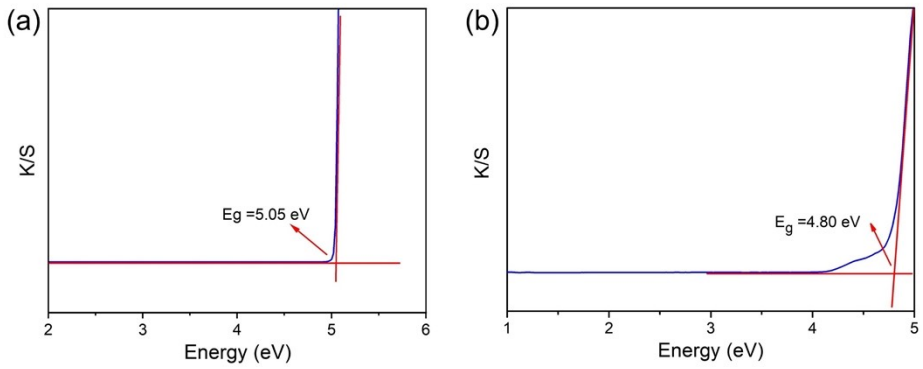

Fig. S3 Experiment band gap for (a) $(C_3N_6H_7)BF_4 \cdot H_2O$ and (b) $(C_3N_6H_7)SO_3CH_3 \cdot H_2O$.

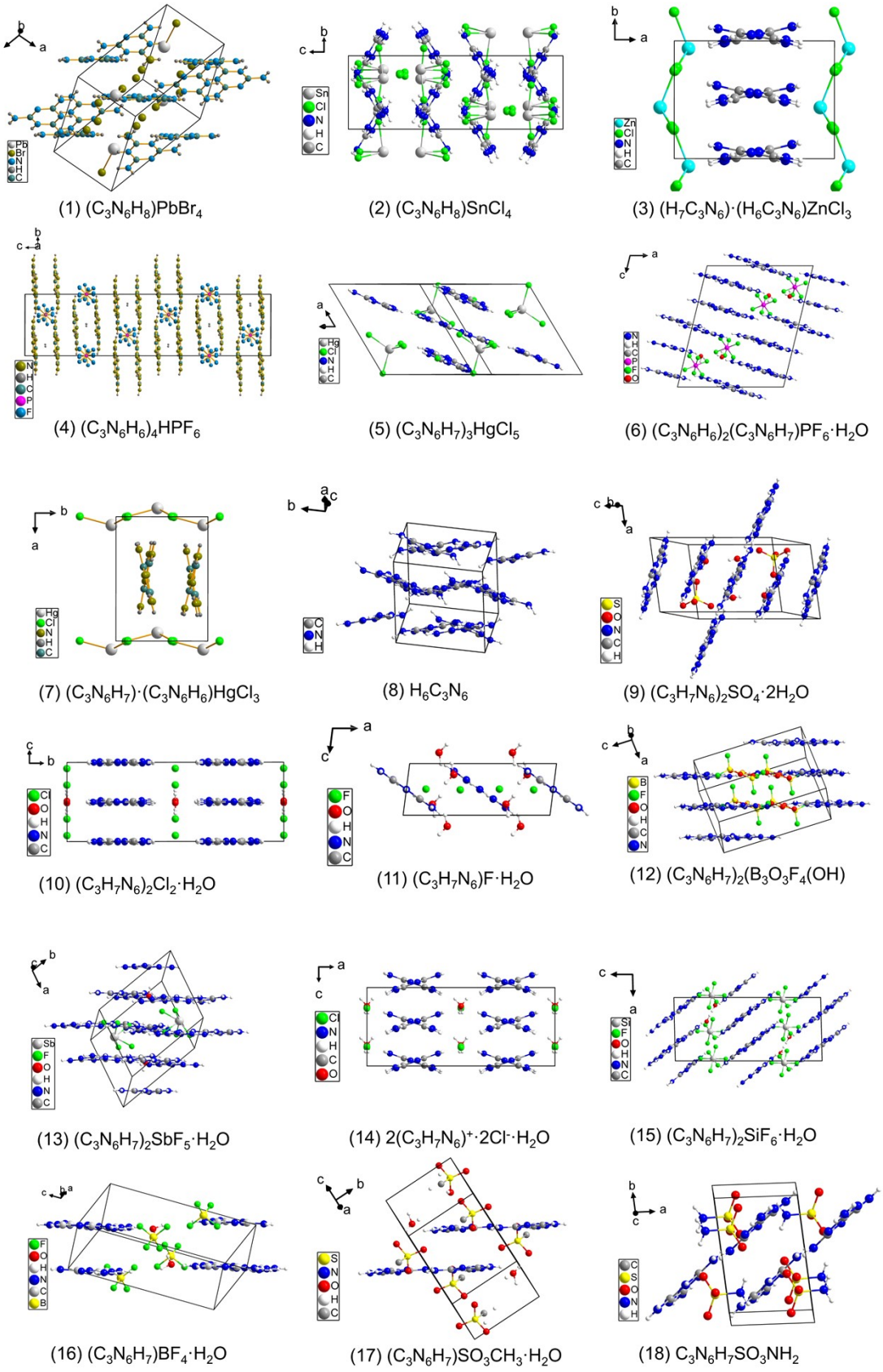

Fig. S4 Comparisons of the orientation of $[C_3H_7N_6]^+$ groups in reported compounds.

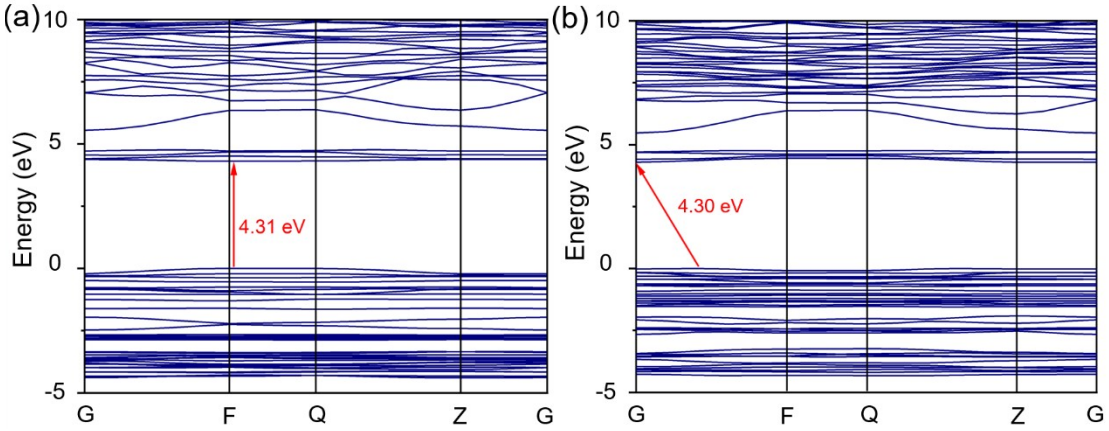

Fig. S5 Electronic band structures for (a) $(C_3N_6H_7)BF_4 \cdot H_2O$ and (b) $(C_3N_6H_7)SO_3CH_3 \cdot H_2O$.

Table S1. Crystallographic data for $(C_3N_6H_7)BF_4 \cdot H_2O$ and $(C_3N_6H_7)SO_3CH_3 \cdot H_2O$.

Empirical formula	**$(C_3N_6H_7)BF_4 \cdot H_2O$**	**$(C_3N_6H_7)BF_4 \cdot H_2O$**	**$(C_3N_6H_7)SO_3CH_3 \cdot H_2O$**
Formula weight	231.97	231.97	240.026
Temperature/K	153	298	298
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P	P	P
a/Å	5.5980(9)	5.7474(7)	6.5998(9)
b/Å	7.4799(13)	7.4778(9)	6.7955(9)
c/Å	11.727(2)	11.7695(14)	12.2611(15)
α/°	102.107(6)	101.789(5)	76.662(5)
β/°	94.096(6)	94.130(5)	85.122(4)
γ/°	110.999(6)	110.156(5)	71.706(4)
Volume/Å^3	442.40(13)	459.22(10)	507.97(12)
Z	2	2	2
$\rho_{calc.}$ / g/cm^3	1.741	1.678	1.571
μ/mm^{-1}	0.182	0.175	0.328
F(000)	236	236	252
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2*θ* range/°	1.799 to 25.337	1.789 to 25.342	3.414 to 50.734
Index ranges	$-6 \le h \le 6$, $-8 \le k \le 8$, $-14 \le l \le 14$	$-6 \le h \le 6$, $-8 \le k \le 8$, $-14 \le l \le 14$	$-7 \le h \le 7$, $-8 \le k \le 8$, $-14 \le l \le 14$
Reflns collected	5462	6159	8526
Unique reflns (R_{int})	1594 [R_{int} = 0.0525]	1644 [R_{int} = 0.0408]	1845 [R_{int} = 0.0870]
Data/restraints/param	1594 / 0 / 140	1644/4/186	1845/0/141
Goodness-of-fit on F^2	1.151	1.039	1.061
R_1[a)]/ wR_2[b)] [I>=2σ (I)]	0.0415/0.1026	0.0526/0.1314	0.0494/0.1146
R_1[a)]/ wR_2[b)] [all data]	0.0457/0.1076	0.0695/0.1480	0.0656/0.1323
Largest diff. peak/hole / e Å^{-3}	0.43/-0.44	0.28/-0.24	0.45/-0.37

[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. The fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(C_3N_6H_7)BF_4 \cdot H_2O$.

Atom	x	y	z	U(eq)
C(1)	2909(3)	8601(2)	7925(2)	18(1)
C(2)	2061(3)	7934(2)	9688(2)	19(1)
C(3)	4392(3)	6428(3)	8662(2)	19(1)
N(1)	2811(3)	9497(2)	7078(1)	25(1)
N(2)	1792(3)	8903(2)	8863(1)	20(1)
N(3)	1018(3)	8250(2)	10650(1)	23(1)
N(4)	3328(3)	6688(2)	9622(1)	20(1)
N(5)	5657(3)	5229(2)	8501(1)	25(1)
N(6)	4246(3)	7382(2)	7805(1)	20(1)
B(1)	11067(4)	7698(3)	3696(2)	22(1)
F(1)	10915(2)	6349(2)	2640(1)	27(1)
F(2)	11740(2)	9560(2)	3481(1)	33(1)
F(3)	8691(2)	7178(2)	4065(1)	43(1)
F(4)	12948(3)	7715(2)	4540(1)	40(1)
O(1)	6889(3)	6214(2)	6134(1)	29(1)

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Table S3. Bond lengths [Å] and angles [°] for $(C_3N_6H_7)BF_4 \cdot H_2O$.

Atom- Atom	Length[Å]	Atom- Atom- Atom	Angle[°]
C1-N1	1.317(2)	C(1)-N(2)-C(2)	115.96(14)
C1-N2	1.322(2)	C(3)-N(4)-C(2)	115.72(14)
C1-N6	1.364(2)	C(3)-N(6)-C(1)	119.24(15)
C2-N2	1.355(2)	F(2)-B(1)-F(1)	108.18(15)
C2-N3	1.323(2)	F(3)-B(1)-F(1)	109.67(16)
C2-N4	1.353(2)	F(3)-B(1)-F(2)	108.90(15)
C3-N4	1.322(2)	F(3)-B(1)-F(4)	111.03(16)
C3-N5	1.321(2)	F(4)-B(1)-F(1)	109.05(15)
C3-N6	1.363(2)	F(4)-B(1)-F(2)	109.97(16)
B1-F1	1.400(2)	N(1)-C(1)-N(2)	121.07(15)
B1-F2	1.389(2)	N(1)-C(1)-N(6)	117.44(15)
B1-F3	1.374(2)	N(2)-C(1)-N(6)	121.47(15)
B1-F4	1.387(2)	N(3)-C(2)-N(2)	117.20(15)
		N(3)-C(2)-N(4)	117.00(15)
		N(4)-C(2)-N(2)	125.79(15)
		N(4)-C(3)-N(6)	121.79(15)
		N(5)-C(3)-N(4)	120.82(16)
		N(5)-C(3)-N(6)	117.38(16)

Table S4. Hydrogen bonds for $(C_3N_6H_7)BF_4 \cdot H_2O$.

D-H	d(D-H)	d(H...A)	d(D...A)	∠DHA
O(1)-H(1C)...F(3)	0.87	2.03	2.8266(18)	150.9
N(6)-H(6)...O(1)	0.88	1.88	2.7231(19)	158.9
N(5)-H(5B)...F(1)#1	0.88	2.20	2.8621(19)	132.2

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

Table S5. The fractional atomic coordinates ($\times 10^4$) and equivalent isotropic

displacement parameters ($Å^2 \times 10^3$) for $(C_3N_6H_7)SO_3CH_3 \cdot H_2O$.

Atom	x	y	z	U(eq)
C1	7515(4)	5336(4)	3876(2)	30.3(7)
C2	4840(4)	4269(4)	3258(2)	31.3(7)
C3	6876(4)	2272(4)	4752(2)	30.7(7)
C4	8091(6)	2833(6)	701(3)	52.3(9)
N1	5951(4)	5683(4)	3139(2)	32.6(6)
N2	5309(4)	2507(4)	4045(2)	33.0(6)
N3	7974(4)	3663(4)	4719.0(19)	30.4(6)
N4	8545(4)	6762(4)	3725(2)	40.4(7)
N5	3293(4)	4719(4)	2539(2)	43.1(7)
N6	7360(4)	526(4)	5544(2)	39.4(7)
O1	10244(4)	2412(5)	2439(2)	62.3(8)
O2	10542(4)	-742(4)	1789(2)	65.3(8)
O3	12159(4)	1827(4)	741(2)	58.3(7)
O4	5929(4)	8762(5)	1365(2)	73.1(10)
S1	10402.4(12)	1470.5(12)	1483.3(6)	38.1(3)

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Table S6. Bond lengths [Å] and angles [°] for $(C_3N_6H_7)SO_3CH_3 \cdot H_2O$.

Atom- Atom	Length[Å]	Atom	Angle[°]
C1-N1	1.358(4)	C1-N3-C3	115.4(2)
C1-N3	1.322(4)	C2-N1-C1	119.5(3)
C1-N4	1.321(4)	C2-N2-C3	115.7(2)
C2-N1	1.357(4)	N2-C2-N1	121.5(3)
C2-N2	1.321(4)	N2-C2-N5	121.6(3)
C2-N5	1.322(4)	N3-C1-N1	121.7(3)
C3-N2	1.354(4)	N3-C3-N2	126.0(3)
C3-N3	1.352(4)	N4-C1-N1	117.1(3)
C3-N6	1.318(4)	N4-C1-N3	121.2(3)
S1-C4	1.748(3)	N5-C2-N1	116.9(3)
S1-O1	1.441(3)	N6-C3-N2	116.5(3)
S1-O2	1.438(3)	N6-C3-N3	117.5(3)
S1-O3	1.458(2)	O1-S1-C4	107.18(17)
		O1-S1-O3	111.02(17)
		O2-S1-C4	108.28(18)
		O2-S1-O1	112.98(18)
		O2-S1-O3	111.60(16)
		O3-S1-C4	105.35(17)

Table S7. Hydrogen bonds for $(C_3N_6H_7)SO_3CH_3 \cdot H_2O$.

D-H	d(D-H)	d(H...A)	d(D...A)	∠DHA
N1-H1...O4	0.8700	1.803(4)	2.645(4)	162.09(11)
N5-H5A...O1#3	0.8700	2.087(4)	2.938(4)	165.82(11)
O4-H4F...O3#1	0.8599	1.880(10)	2.729(4)	169(5)
O4-H4G...O3#2	0.8598	1.994(12)	2.833(4)	165(4)

Symmetry transformations used to generate equivalent atoms: #1+0 #2 x+2,y+1,z #3+0

Table S8. Comparisons of the $[C_3N_6H_7]^+$ density, optical properties in reported compounds.

No	Species	Band gap (eV)	Density ($\times 10^{-3}$ Å)	Birefringence (@546 nm)[c]	UV Cut-off(nm)
1	$(C_3N_6H_8)PbBr_4$[1]	3.13[e]	3.14	0.29@550nm	374
2	$(C_3N_6H_8)SnCl_4$[2]	3.71[e]	3.45	0.34@550nm	334
3	$(H_7C_3N_6)\cdot(H_6C_3N_6)ZnCl_3$[3]	3.95[e]	5.35	0.26@1064nm	236
4	$(C_3N_6H_6)_4HPF_6$[4]	4.12[e]	4.57	0.26	300
5	$(C_3N_6H_7)_3HgCl_5$[5]	4.19[e]	3.38	0.093 @1064nm	290
6	$(C_3N_6H_6)_2(C_3N_6H_7)PF_6\cdot H_2O$[4]	4.20[e]	5.77	0.24	300
7	$(C_3N_6H_7)\cdot(C_3N_6H_6)HgCl_3$[5]	4.40[e]	5.23	0.25@1064nm	278
8	$H_6C_3N_6$[6]	4.60[e]	7.73	0.26	248
9	$(C_3H_7N_6)_6(H_2PO_4)_4\ (HPO_4)\cdot 4H_2O$[7]	4.6[e]	/	0.22@1064nm	/
10	$(C_3H_7N_6)_2SO_4\cdot 2H_2O$[7]	4.62[e]	5.25	/	/
11	$(C_3H_7N_6)_2Cl_2\cdot H_2O$[6]	4.70[e]	5.63	0.33@550nm	230
12	$(C_3H_7N_6)F\cdot H_2O$[6]	4.72[e]	6.00	0.38@550nm	220
13	$(C_3N_6H_7)_2(B_3O_3F_4(OH)$[8]	4.72[e]	4.98	0.44	240
14	$(C_3N_6H_7)_2SbF_5\cdot H_2O$[9]	4.74[e]	4.89	0.38@550nm	220
15	$2(C_3H_7N_6)^+\cdot 2Cl^-\cdot H_2O$[10]	4.75[e]	5.58	0.28	245
16	$(C_3N_6H_7)_2SiF_6\cdot H_2O$[11]	4.76[e]	5.31	0.15@550nm	220
17	**$(C_3N_6H_7)SO_3CH_3\cdot H_2O$**	4.80[e]	3.94	0.31	233
18	**$(C_3N_6H_7)BF_4\cdot H_2O$**	5.05[e]	3.39	0.37	244
19	$C_3N_6H_7SO_3NH_2$[12]	5.53[e]	3.20	0.34	206

Note: Upper corner "e" is the experimental value, upper corner "c" is the theoretical calculation value.

References

1. W. Q. Huang, X. Zhang, Y. Q. Li, Y. Zhou, X. Chen, X. Q. Li, F. F. Wu, M. C. Hong, J. H. Luo and S. G. Zhao, A hybrid halide perovskite birefringent crystal, *Angew. Chem. Int. Ed.*, 2022, **61**, e202202746.
2. W. Q. Huang, X. L. Wu, B. Ahmed, Y. Q. Li, Y. Zhou, H. Wang, Y. P. Song, X. J. Kuang, J. H. Luo and S. G. Zhao, A hybrid halide lead-free pseudo-perovskite with large birefringence, *Inorg. Chem. Front.*, 2023, **10**, 2039.
3. L. H. Liu, Z. Y. Bai, L. Hu, D. S. Wei, Z. B. Lin and L. Z. Zhang, A melamine-based organic–inorganic hybrid material revealing excellent optical performance and moderate thermal stability, *J. Mater. Chem. C*, 2021, **9**, 7452.
4. L. H. Liu, F. F. Yuan, Y. S. Huang, Z. B. Lin and L. Z. Zhang, Two UV optical crystals with strong optical anisotropy, large band gaps and an alpha-BBO type structure, *Dalton Trans*, 2023, **52**, 5798.
5. Z. Y. Bai, J. Lee, H. Kim, C. L. Hu and K. M. Ok, Unveiling the superior optical properties of novel melamine-based nonlinear optical material with strong second-harmonic generation and giant optical anisotropy, *Small*, 2023, **19**, 2301756.
6. Y. G. Shen, L. Ma, G. F. Dong, H. L. Yu and J. H. Luo, β-$(C_3H_7N_6)_2Cl_2\cdot H_2O$ and $(C_3H_7N_6)F\cdot H_2O$: two UV birefringent crystals induced by uniformly aligned structural groups, *Inorg. Chem. Front.*, 2023, **10**, 2022.
7. S. F. Li, L. Hu, Y. Ma, F. F. Mao, J. Zheng, X. D. Zhang and D. Yan, Noncentrosymmetric $(C_3H_7N_6)_6(H_2PO_4)_4(HPO_4)\cdot 4H_2O$ and centrosymmetric $(C_3H_7N_6)_2SO_4\cdot 2H_2O$: exploration of acentric structure by combining planar and tetrahedral motifs via hydrogen bonds, *Inorg. Chem.*,

2022, **61**, 10182.

8. C. C. Jin, F. M. Li, Z. H. Yang, S. L. Pan and M. Mutailipu, $[C_3N_6H_7]_2[B_3O_3F_4(OH)]$: a new hybrid birefringent crystal with strong optical anisotropy induced by mixed functional units, *J. Mater. Chem. C*, 2022, **10**, 6590.
9. Y. G. Shen, B. Chen, H. Chen and J. H. Luo, $(C_3N_6H_7)_2SbF_5 \cdot H_2O$ exhibiting strong optical anisotropy from the optimal arrangement of π-conjugated $(C_3N_6H_7)^+$ groups, *Inorg. Chem.*, 2022, **61**, 14242.
10. L. H. Liu, C. L. Hu, Z. Y. Bai, F. F. Yuan, Y. S. Huang, L. Z. Zhang and Z. B. Lin, $2(C_3H_7N_6)^+.2Cl^- .H_2O$: an ultraviolet nonlinear optical crystal with large birefrigence and strong second-harmonic generation, *Chem. Commun.*, 2020, **56**, 14657.
11. Y. G. Shen, Y. W. Zhou, X. L. Xue, H. L. Yu, S. G. Zhao and J. H. Luo, $(C_3N_6H_7)_2SiF_6 \cdot H_2O$: an ultraviolet birefringent crystal exceeding the intrinsic energy gap of an organic reagent, *Inorg. Chem. Front.*, 2022, **9**, 5226.
12. D. Y. Dou, Q. Shi, Y. J. Bai, C. Chen, B. B. Zhang and Y. Wang, $C_3N_6H_7SO_3NH_2$: non-π-conjugated tetrahedra decoupling π-conjugated groups achieving large optical anisotropy and wide band gap, *Mater. Chem. Front.*, 2023, **7**, 5924.