**Supporting Information**

# $(C_5N_2H_7)IO_2F_2$ and $(C_3N_6H_8)(IO_2F_2)_2$ : Two new organic-inorganic hybrid fluoroiodate birefringent crystals

Si Yuan [a,b] Chun-Li Hu,[b] and Jiang-Gao Mao *[a,b]

a State Key Laboratory of Functional Crystals and Devices, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China, Email: mjg@fjirsm.ac.cn

b School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, P. R. China.

* Corresponding Author: mjg@fjirsm.ac.cn

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**Table S1** Crystallographic data for $(C_5N_2H_7)IO_2F_2$ and $(C_3N_6H_8)(IO_2F_2)_2$

| **Formula** | **$(C_5N_2H_7)IO_2F_2$** | **$(C_3N_6H_8)(IO_2F_2)_2$** |
|---|---|---|
| Formula weight | 292.03 | 521.95 |
| Temperature (K) | 100 (2) | 100 (2) |
| Crystal system | monoclinic | monoclinic |
| Space group (number) | $C2/m$ (12) | $C2/c$ (15) |
| $a$ (Å) | 7.4919(3) | 19.8063(7) |
| $b$ (Å) | 17.6990(6) | 8.0742(3) |
| $c$ (Å) | 6.3050(2) | 7.2996(3) |
| α (deg) | 90 | 90 |
| β (deg) | 98.893(3) | 96.819(3) |
| γ (deg) | 90 | 90 |
| Volume (Å$^3$) | 825.99(5) | 1159.09(8) |
| $Z$ | 4 | 4 |
| $\rho_{calc}$ (g/cm$^3$) | 2.348 | 2.991 |
| $\mu$ (mm$^{-1}$) | 3.874 | 5.505 |
| $F$(000) | 552 | 968 |
| λ (Mo-$K_\alpha$) | 0.71073 Å | 0.71073 Å |
| Goodness-of-fit on $F^2$ | 1.175 | 1.217 |
| Final $R$ indexes [$I \geq 2\sigma(I)$][a] | $R_1$ = 0.0169, w$R_2$ = 0.0413 | $R_1$ = 0.0188, w$R_2$ = 0.0493 |
| Final $R$ indexes (all data)[a] | $R_1$ = 0.0174, w$R_2$ = 0.0415 | $R_1$ = 0.0198, w$R_2$ = 0.0498 |

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and $wR_2 = \{\Sigma w[(F_o)^2 - (F_c)^2]^2 / \Sigma w[(F_o)^2]^2\}^{1/2}$

**Table S2** Selected bond lengths (Å) for $(C_5N_2H_7)IO_2F_2$ and $(C_3N_6H_8)(IO_2F_2)_2$

| **$(C_5N_2H_7)IO_2F_2$** | | | |
|---|---|---|---|
| **Atom–Atom** | **Length [Å]** | **Atom–Atom** | **Length [Å]** |
| I1–F1$^{\#1}$ | 1.972(2) | N2–C4 | 1.341(6) |
| I1–F1 | 1.972(2) | C1–C6 | 1.410(8) |
| I1–O1 | 1.782(2) | C1–C2 | 1.416(8) |
| I1–O2 | 1.783(2) | C2–C4 | 1.379(8) |
| N1–C1 | 1.334(5) | C3–C6 | 1.377(8) |
| N2–C3 | 1.327(7) | | |
| **$(C_3N_6H_8)(IO_2F_2)_2$** | | | |
| **Atom–Atom** | **Length [Å]** | **Atom–Atom** | **Length [Å]** |
| I1–O2 | 1.784(2) | I1–F2 | 2.0863(17) |
| I1–O1 | 1.787(2) | N1–C1 | 1.338(4) |
| I1–F1 | 1.9426(19) | N1–C2 | 1.372(4) |

| | | | |
|---|---|---|---|
| N2–C2 | 1.330(4) | N3–C1 | 1.320(6) |
| N2–C2$^{\#1}$ | 1.330(4) | N4–C2 | 1.318(4) |

Symmetry transformations used to generate equivalent atoms:

For $(C_5N_2H_7)IO_2F_2$:

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

For $(C_3N_6H_8)(IO_2F_2)_2$:

#1: 1-x, +y, 3/2-z

**Table S3** Selected bond angles for $(C_5N_2H_7)IO_2F_2$ and $(C_3N_6H_8)(IO_2F_2)_2$

| **$(C_5N_2H_7)IO_2F_2$** | | | |
|---|---|---|---|
| **Atom–Atom–Atom** | **Angle [°]** | **Atom–Atom–Atom** | **Angle [°]** |
| O1–I1–O2 | 101.78(11) | C3–N2–C4 | 121.6(5) |
| O1–I1–F1$^{\#1}$ | 91.41(5) | N1–C1–C6 | 126.7(5) |
| O2–I1–F1$^{\#1}$ | 89.69(5) | N1–C1–C2 | 115.4(5) |
| O1–I1–F1 | 91.41(5) | C6–C1–C2 | 117.7(5) |
| O2–I1–F1 | 89.69(5) | C4–C2–C1 | 120.6(9) |
| F1$^{\#1}$–I1–F1 | 177.18(10) | N2–C3–C6 | 122.7(7) |
| N2–C4–C2 | 119.4(7) | C3–C6–C1 | 118.0(8) |
| **$(C_3N_6H_8)(IO_2F_2)_2$** | | | |
| **Atom–Atom–Atom** | **Angle [°]** | **Atom–Atom–Atom** | **Angle [°]** |
| F1–I1–F2 | 177.66(7) | C2$^{\#1}$–N2–C2 | 115.8(4) |
| O1–I1–F2 | 86.52(9) | N1$^{\#1}$–C1–N1 | 117.4(4) |
| O1–I1–F1 | 91.17(10) | N3–C1–N1 | 121.3(2) |
| O2–I1–F2 | 89.75(9) | N3–C1–N1$^{\#1}$ | 121.3(2) |
| O2–I1–F1 | 90.64(9) | N2–C2–N1 | 122.7(3) |
| O2–I1–O1 | 98.32(10) | N4–C2–N1 | 116.7(3) |
| C2–N1–C1 | 120.4(3) | N4–C2–N2 | 120.7(3) |

Symmetry transformations used to generate equivalent atoms:

For $(C_5N_2H_7)IO_2F_2$:

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

For $(C_3N_6H_8)(IO_2F_2)_2$:

#1: 1-x, +y, 3/2-z

**Table S4** Hydrogen bond lengths (Å) for $(C_5N_2H_7)IO_2F_2$ and $(C_3N_6H_8)(IO_2F_2)_2$

| **$(C_5N_2H_7)IO_2F_2$** | | | | |
|---|---|---|---|---|
| **D—H…A** | **d(D-H)** | **d(H…A)** | **d(D…A)** | **∠(D-H…A)(°)** |
| N(1)-H(1)…O(2)$^{\#2}$ | 0.900 | 2.05(6) | 2.893(3) | 156.0 |
| N(2)-H(2)…O(1) | 0.88 | 2.21 | 3.003(5) | 150 |
| **$(C_3N_6H_8)(IO_2F_2)_2$** | | | | |
| **D—H…A** | **d(D-H)** | **d(H…A)** | **d(D…A)** | **∠(D-H…A)(°)** |
| N(1)-H(1A)…O(1) | 0.88 | 1.78 | 2.638(3) | 165.3 |

| | | | | |
|---|---|---|---|---|
| N(3)-H(3A)…F(2) | 0.90 | 1.97 | 2.869(3) | 175.4 |
| N(4)-H(4A)...F(2)$^{\#1}$ | 0.88 | 1.93 | 2.806(3) | 170.2 |

Symmetry transformations used to generate equivalent atoms:

For $(C_5N_2H_7)IO_2F_2$:

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

For $(C_3N_6H_8)(IO_2F_2)_2$:

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

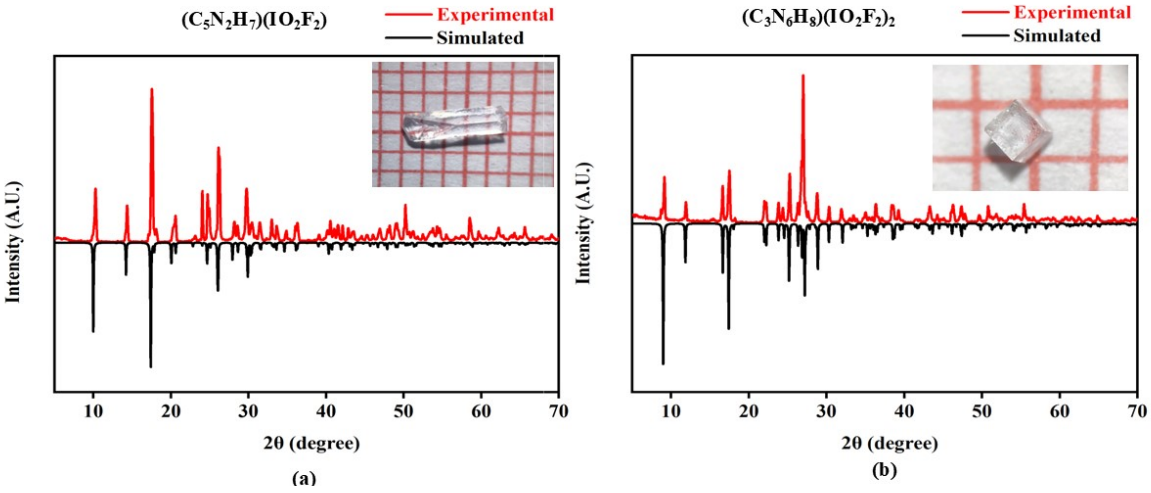



**Figure S1** Simulated and experimental powder X-ray diffraction patterns of (a)$(C_5N_2H_7)IO_2F_2$ and (b)$(C_3N_6H_8)(IO_2F_2)_2$

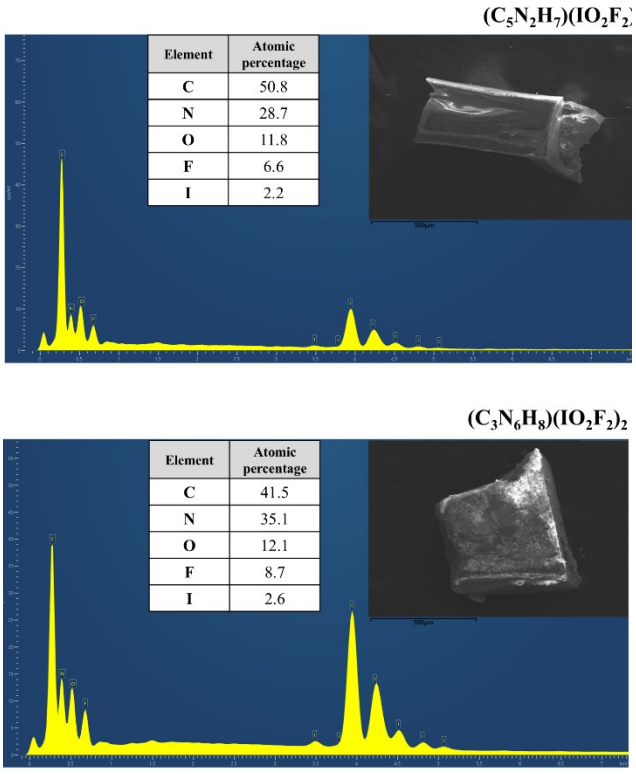



**Figure S2** Energy dispersive spectrum for $(C_5N_2H_7)IO_2F_2$ and $(C_3N_6H_8)(IO_2F_2)_2$

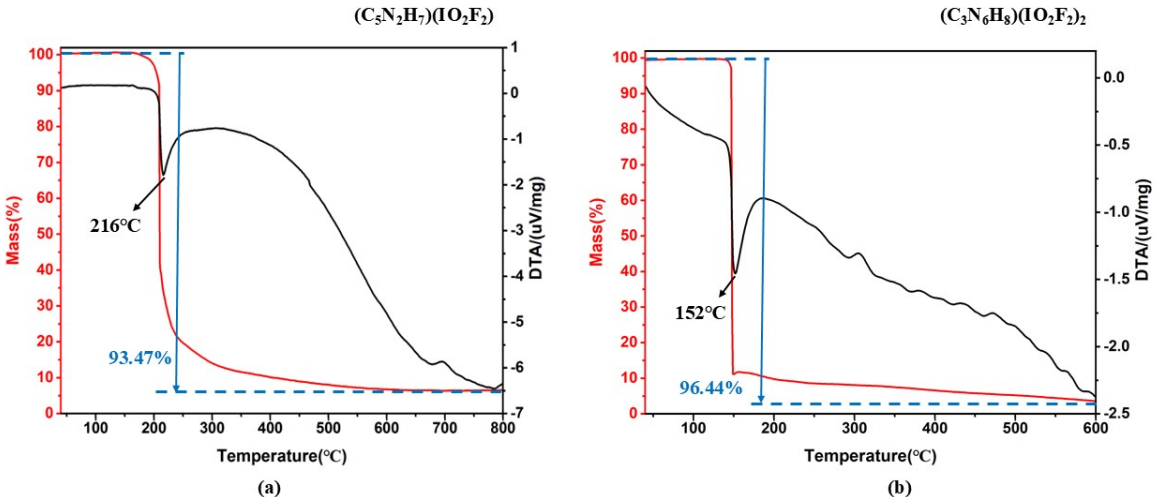



**Figure S3** TGA and DTA curves of (a)$(C_5N_2H_7)IO_2F_2$ and (b)$(C_3N_6H_8)(IO_2F_2)_2$ under the $N_2$ atmosphere.

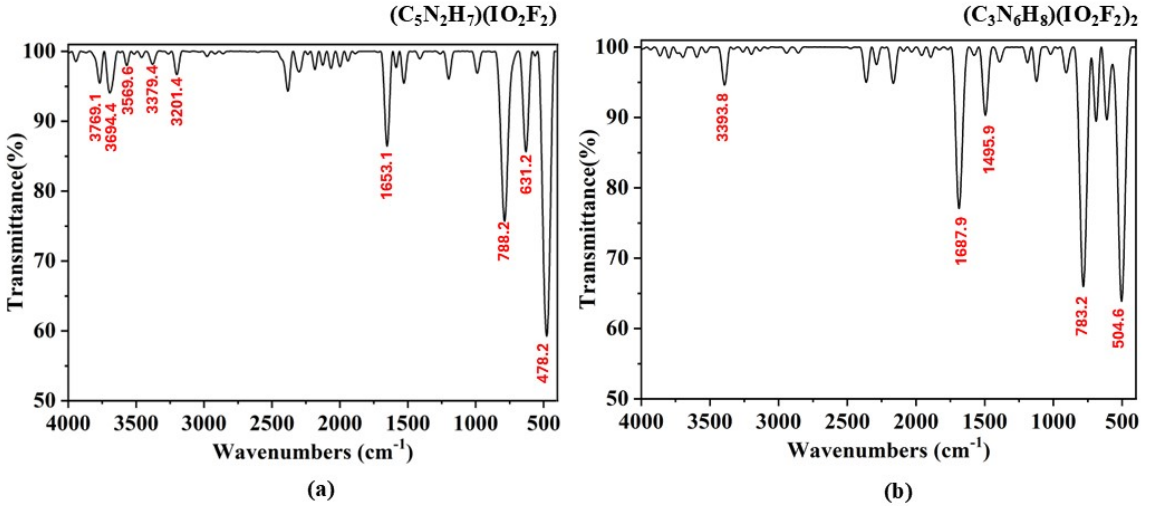



**Figure S4.** IR spectra for (a)$(C_5N_2H_7)IO_2F_2$ and (b)$(C_3N_6H_8)(IO_2F_2)_2$

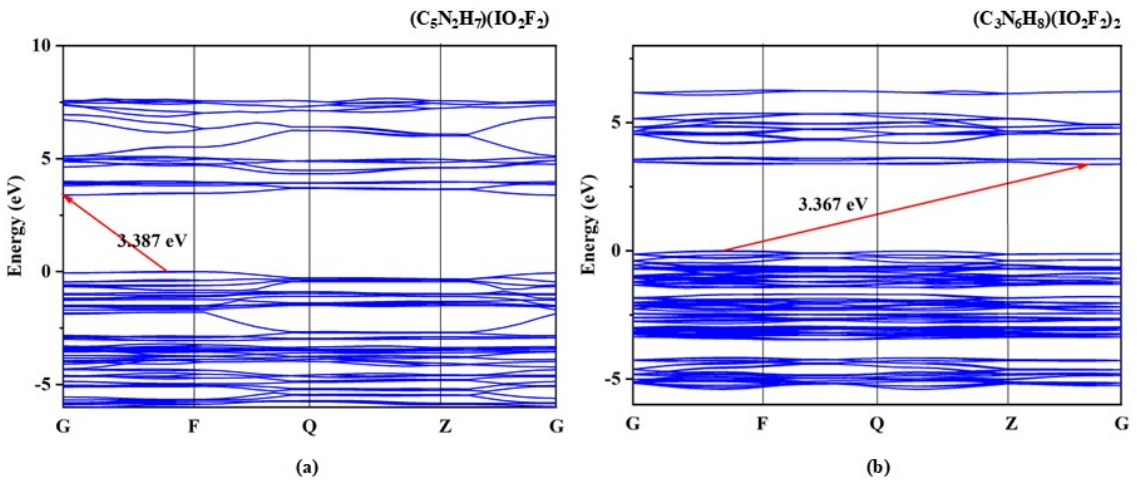



**Figure S5** The calculated band structure of (a)$(C_5N_2H_7)IO_2F_2$ and (b)$(C_3N_6H_8)(IO_2F_2)_2$.

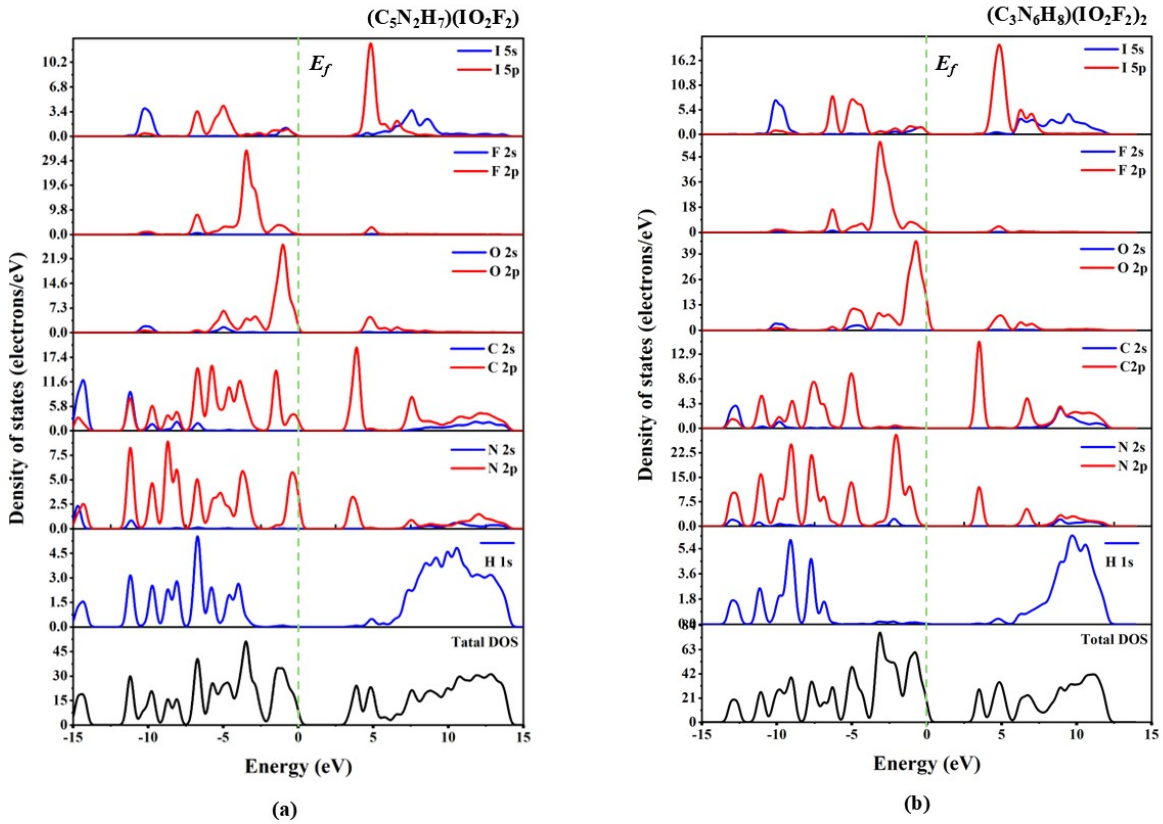



**Figure S6.** The partial and total density of states for (a)$(C_5N_2H_7)IO_2F_2$ and (b)$(C_3N_6H_8)(IO_2F_2)_2$.

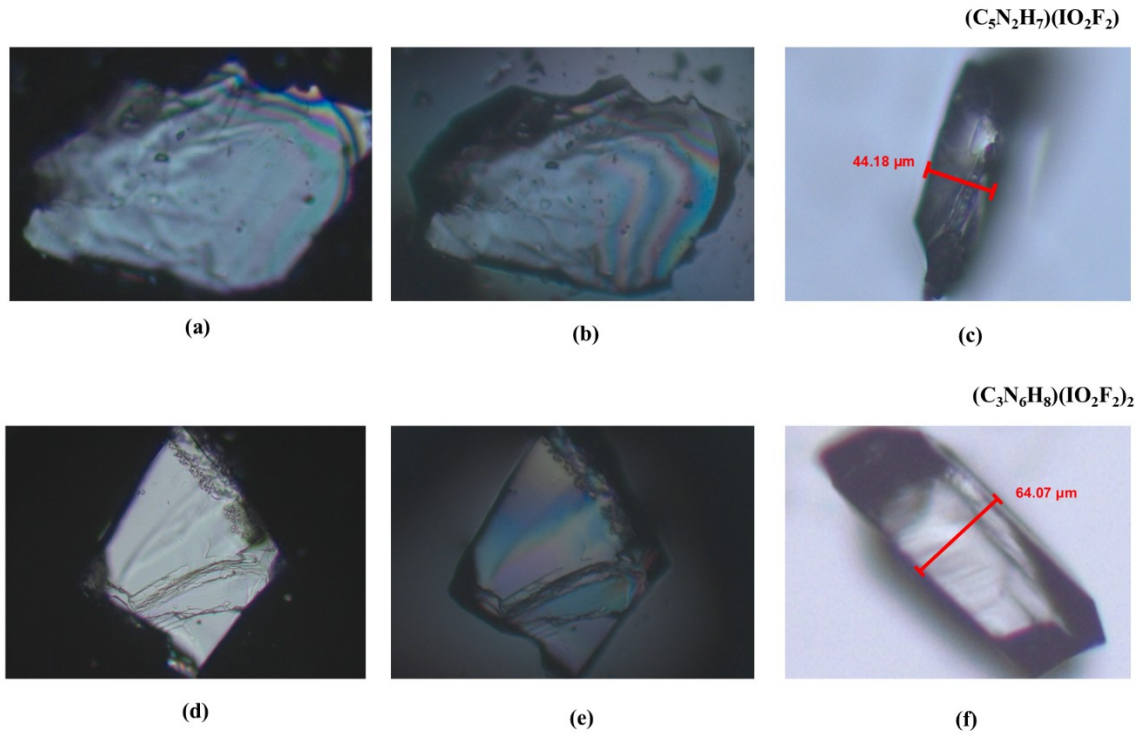
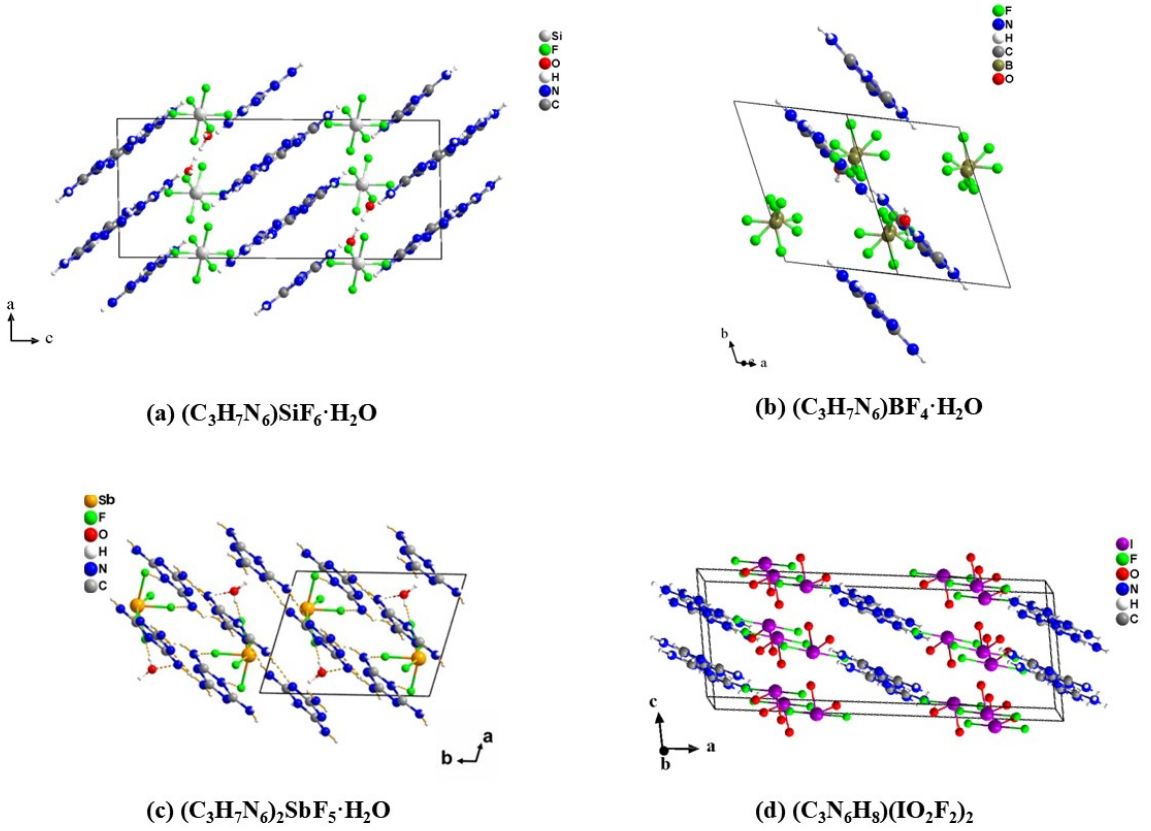



**Figure S7** Experimental birefringence at 550 nm for (a-c)$(C_5N_2H_7)IO_2F_2$ and (d-f)$(C_3N_6H_8)(IO_2F_2)_2$.




**(a) $(C_3H_7N_6)SiF_6 \cdot H_2O$** **(b) $(C_3H_7N_6)BF_4 \cdot H_2O$**

**(c) $(C_3H_7N_6)_2SbF_5 \cdot H_2O$** **(d) $(C_3N_6H_8)(IO_2F_2)_2$**

**Figure S8** Comparison of organic ring arrangement in melamine-containing organic-inorganic hybrid birefringence crystals with that of $(C_3N_6H_8)(IO_2F_2)_2$