Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

An Organic-Inorganic Hybrid Birefringent Material with Diverse Functional Groups

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Experimental Procedures

Single-Crystal Structure Determination.

A colorless $(CN_4H_7)SbC_2O_4F_2(H_2O)_{0.5}$ (**CN_4SCOF**) crystal (0.10 × 0.06 × 0.05 mm^3) suitable for structure determination of title compounds were mounted on a Bruker D8 equipped with Mo Kα radiation (λ = 0.71073 Å), and 200(2)K diffraction data were collected. The data reduction and absorption corrections were carried out with the program APEX3. The structure was solved by the direct method with program SHELXS and refined with the least-squares program SHELXL.[1] Final refinements include anisotropic displacement parameters. The structure was checked for missing symmetry elements using program PLATON,[2] and no higher symmetry was found. Details of crystal parameters, data collection, and structure refinement are summarized in Table S1. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table S2. The selected bond distances and angles are presented in Table S3, and the anisotropic displacement parameters are listed in Table S4.

Elemental Analysis.

Semiquantitative microprobe analyses on the **CN_4SCOF** crystal were performed with the aid of a field emission scanning electron microscope (Nova NanoSEM 230) equipped with an energy dispersive X-ray spectroscope (EDX). The energy dispersive spectra were collected on visibly clean surfaces of the samples, and confirmed the presence of N, Sb, C and F, which is well consistent with that determined by single-crystal XRD analysis.

Thermal Stability.

The thermal stability was investigated by the thermogravimetry (TG) and the differential thermal analysis (DTA) on a simultaneous NETZSCH STA 449C thermal analyzer in an atmosphere of flowing N_2. About 8.65 mg powders of **CN_4SCOF** was placed into an Al_2O_3 crucible, heated at a rate of 10 K min^{-1} from room temperature to 1000 K.

UV-Vis-NIR Diffuse Reflectance Spectroscopy.

The UV-Vis-NIR diffuse reflection data were recorded at room temperature using a powdered $BaSO_4$ sample as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV/Vis/NIR spectrophotometer. The scanning wavelength range is from 200 nm to 800 nm. Absorption (K/S) data were calculated from the following Kubelka-Munk function:[3]

$$F(R) = (1-R)^2/(2R) = K/S$$

where R is the reflectance, K is the absorption, and S is the scattering. In the (K/S) versus E plot, extrapolating the linear portion of the rising curve to zero gives rise to the onset of absorption.

Powder XRD Analysis.

Powder X-ray diffraction measurements of the CN_4SCOF sample was carried out with a Miniflex 600 diffractometer equipped with an incident beam monochromator set for Cu Kα radiation (λ = 1.5418 Å). The 2θ range was 7-77° with a scan step width of 0.02° and a fixed counting time of 0.40 s/step.

Birefringence Measurements.

The birefringence of CN_4SCOF was characterized by using the polarizing microscope equipped (ZEISS Axio Scope. A1) with Berek compensator. The wavelength of the light source was 546 nm. Owing to the clear boundary lines of the first-, second- and third-order interference color, the relative error was small enough. Before the scanning, the small and transparent CN_4SCOF lamellar crystals were chosen to measure, in order to improve the accuracy of the birefringence. The formula for calculating the birefringence is listed below,

$$R = | N_e - N_o | \times T = \Delta n \times T \qquad \text{Eq. (1)}$$

Here, R represents the optical path difference, Δn means the birefringence, and T denotes the thickness of the crystal.

Computational Methods.

The first-principles calculations of CN_4SCOF were carried out by using the VASP code[4] to understand the relationship between structure and properties, and to analyze the contribution of anion to the birefringence. The generalized gradient approximation (GGA) was adopted, and Perdew-Burke-Ernzerhof (PBE) functional was chosen to calculate the exchange-correlation potential, [5,6] with an energy cutoff of 500 eV for CN_4SCOF. The Brillouin zone was sampled using the Monkhorst-Pack k-point sampling of 5×4×1. The band structure and density of states (DOS)/partial DOS were computed based on the energy and force convergence to 10^{-5} eV and 0.01 eV/Å, respectively. The linear optical properties were examined based on the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of dielectric function ε_2 can be calculated based on the electronic structures and the real part is obtained by the Kramers-Kronig transformation, accordingly the refractive indices and the birefringence (Δn) can be calculated. The frequency-dependent refractive indices were calculated to demonstrate the validity of birefringence Measurements.

Results and Discussion

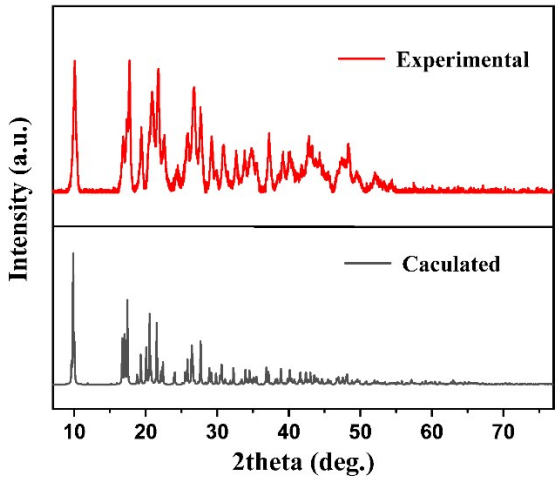

Figure S1. Experimental and calculated XRD patterns of CN_4SCOF.

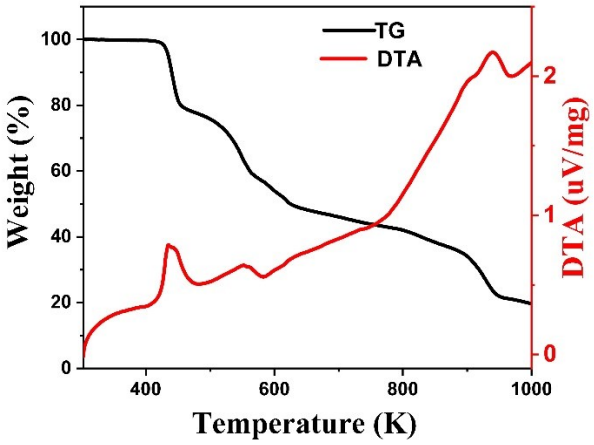

Figure S2. TG and DTA curves of CN_4SCOF.

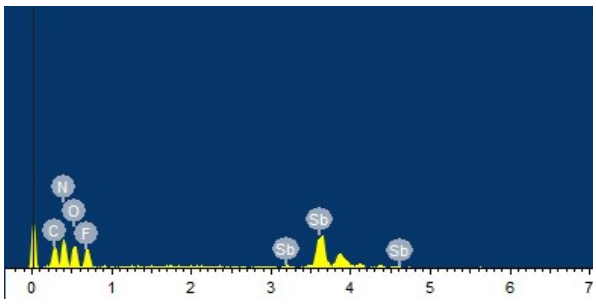

Figure S3. Energy dispersive X-ray spectroscopy result for CN_4SCOF.

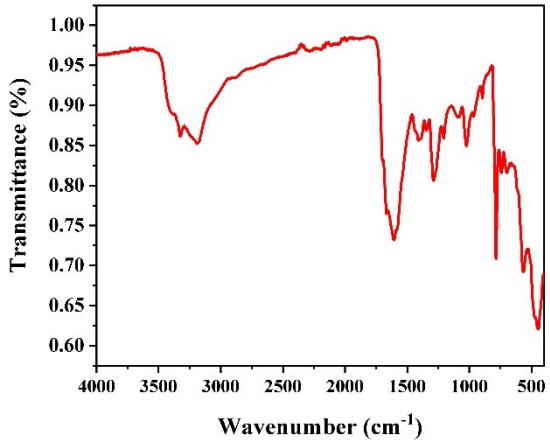

Figure S4. IR spectrum of CN_4SCOF in the range from 400 to 4000 cm^{-1}.

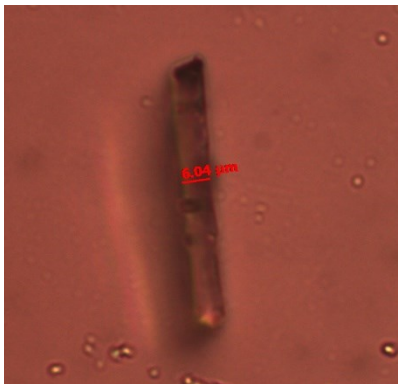

Figure S5. The thickness of CN_4SCOF crystal.

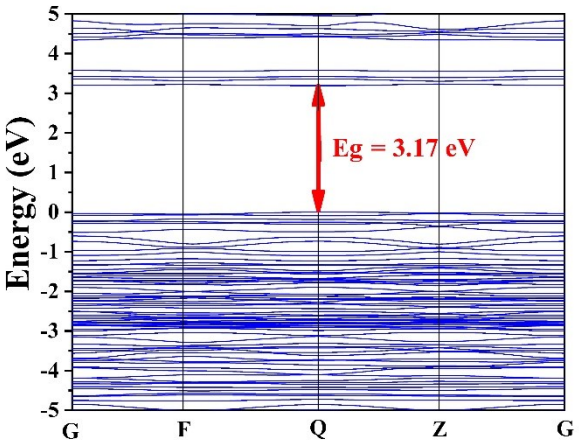

Figure S6. Calucated electronic band structure of CN_4SCOF.

Table S1. The ratio of CHN elements in the CN_4SCOF.

Sample information	**$(CN_4H_7)SbC_2O_4F_2(H_2O)_{0.5}$**
Test requirements	**Vario MICRO**
Test item requirements	**CHN ratio**
Test Results （Mass ratio）	**N=18.78/18.47 C=10.64/10.46 H=2.31/2.27**
Test Results （Molar ratio）	**C:N:H= 1.00 : 1.43 : 2.66**

Table S2. Crystal data and structure refinement for CN_4SCOF.

Formula	**CN_4SCOF**
Formula weight(g/mol)	663.77
Wavelength (Å)	0.71073
Temperature (K)	200.15(2)
Crystal system, space group	triclinic, *P*-1(2)
a (Å)	9.5230(7)
b (Å)	10.6568(8)
c (Å)	10.7489(8)
α(°)	115.937(2)
β (°)	108.831(2)
γ (°)	95.796(3)
Volume ($Å^3$)	890.09(11)
Z, Calculated density (g/cm^3)	2, 2.469
Absorption coefficient (mm^{-1})	3.140
F(000)	632.0
Crystal size (mm)	0.06 × 0.06 × 0.05
Theta range for data collection (deg.)	4.54 to 55.08
Limiting indices	-12<=h<=12, -13<=k<=13, -13<=l<=13
Reflections collected / unique	16067 / 1963 [R(int) = 0.0327]
Data / restraints / parameters	4087 / 1 / 264
Goodness-of-fit on F^2	0.964
Final R indices [I>2sigma(I)][a]	R_1 = 0.0255, wR_2 = 0.1029
R indices (all data)	R_1 = 0.0289, wR_2 = 0.1107
Largest diff. peak and hole($e.A^{-3}$)	0.607 and -1.128

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for CN_4SCOF.

Atom	Wyck.	site	*x*/a	*y*/b	*z*/c	U_{eq} [Å²][a]
Sb1	2i	1	5296.8(7)	6943.4(5)	3380.1(6)	13.4(3)
Sb2	2i	1	10042.7(7)	3148.9(5)	6772.5(6)	13.4(3)
F1	2i	1	9144(7)	3915(5)	5394(5)	24.2(12)
F2	2i	1	7950(6)	2254(6)	6270(6)	25.9(12)
F3	2i	1	7048(6)	7994(5)	3367(6)	21.9(11)
F4	2i	1	6870(7)	6521(5)	4768(6)	25.3(12)
O1	2i	1	5492(7)	11006(7)	6935(6)	17.1(12)
O2	2i	1	5884(7)	8885(6)	5627(7)	18.2(13)
O3	2i	1	5909(8)	4977(7)	1702(7)	21.5(14)
O4	2i	1	5793(8)	3553(7)	-608(7)	24.0(14)
O5	2i	1	9376(8)	6565(7)	10581(8)	23.6(14)
O6	2i	1	9349(9)	5105(8)	8326(8)	22.8(15)
O7	2i	1	9576(8)	1312(6)	4470(7)	17.9(13)
O8	2i	1	9812(7)	-885(7)	3134(7)	17.3(12)
O9	2i	1	6138(7)	3987(7)	4853(7)	28.7(15)
C1	2i	1	5383(9)	9979(9)	5737(9)	14.1(16)
C2	2i	1	5491(10)	4576(9)	311(10)	16.7(17)
C3	2i	1	9628(10)	5475(9)	9685(10)	17.4(17)
C4	2i	1	9833(9)	110(9)	4309(9)	13.9(16)
C5	2i	1	3492(11)	2105(10)	1139(11)	22.1(19)
C6	2i	1	8579(10)	2231(10)	1370(10)	18.3(17)
N1	2i	1	2979(10)	3063(10)	2002(10)	31(2)
N2	2i	1	4575(10)	1592(10)	1744(9)	23.1(18)
N3	2i	1	2920(7)	1643(7)	-320(7)	25.8(18)
N4	2i	1	3521(7)	654(7)	-1236(7)	25.3(17)
N5	2i	1	8072(11)	3148(10)	2227(10)	25.2(19)
N6	2i	1	9701(8)	1731(9)	1945(8)	22.1(17)
N7	2i	1	7963(6)	1759(6)	-101(6)	21.1(16)

Table S4. Selected bond distances (Å) and angles (deg.) for CN_4SCOF.

Sb(2)-F(1)	1.994(5)	Sb(1)-F(3)	1.920(5)
Sb(1)-O(1) #1	2.504(6)	C(4)-O(7)	1.276(10)
Sb(1)-O(2)	2.225(6)	O(3)-O(2)	1.265(11)
Sb(1)-O(3)	2.367(6)	Sb (2)-O(7)	2.243(6)
Sb (2)-F(2)	1.909(5)	O(2)-C(1)	1.276(10)
C(1)-C(1) #1	1.539(16)	O(1)-C(1)	1.234(10)
Sb (2)-O(6)	2.348(7)	C(4)-O(8)	1.236(10)
Sb(2)-O(8)	2.474(6)	N(1)-C(5)	1.307(13)
N(3)-C(5)	1.311(11)	N(5)-C(6)	1.278(13)
N(2)-C(5)	1.332(13)	N(4)-N(3)	1.4083(10)
F3-Sb1-F4	84.8(2)	F3-Sb1-O2	85.5(2)
F4-Sb1-O2	78.1(2)	F3-Sb1-O3	80.1(2)
F4-Sb1-O3	76.8(2)	O2-Sb1-O3	152.1(2)
C6-N7-N8	119.5(5)	C5-N3-N4	119.3(5)
O1-C1-O2	124.9(8)	O8-C4-O7	125.1(7)

Symmetry transformations used to generate equivalent atoms:
#1 1-X,2-Y,1-Z; #2 2-X,-Y,1-Z; #3 2-X,1-Y,2-Z; #4 1-X,1-Y,-Z

Table S5. Anisotropic displacement parameters (Å^2) for CN_4SCOF.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{23}
Sb1	17.2(4)	12.6(4)	11.9(4)	6.6(3)	6.4(3)	6.4(2)
Sb2	16.0(4)	13.6(4)	11.1(4)	6.2(3)	6.1(3)	5.1(2)
F1	37(3)	24(3)	17(2)	14(2)	10(2)	16(2)
F2	34(3)	25(3)	20(3)	13(2)	8(2)	17(2)
F3	21(3)	22(3)	27(3)	13(2)	12(2)	7(2)
F4	34(3)	25(3)	20(3)	13(2)	8(2)	17(2)
O1	23(3)	18(3)	9(3)	5(2)	6(2)	10(2)
O2	28(3)	16(3)	12(3)	7(2)	6(2)	11(3)
O3	29(4)	21(3)	16(3)	10(3)	9(3)	15(3)
O4	36(4)	20(3)	17(3)	8(3)	12(3)	19(3)
O5	36(4)	19(3)	22(3)	11(3)	17(3)	17(3)
O6	35(4)	22(3)	16(3)	11(3)	12(3)	14(3)
O7	30(3)	15(3)	12(3)	8(2)	8(3)	9(3)
O8	25(3)	15(3)	10(3)	4(2)	7(2)	7(2)
O9	26(4)	35(4)	31(4)	21(3)	11(3)	14(3)
C1	17(4)	14(4)	15(4)	8(3)	8(3)	6(3)
C2	20(4)	14(4)	13(4)	5(3)	6(3)	5(3)
C3	22(4)	14(4)	13(4)	4(3)	8(3)	4(3)
C4	16(4)	17(4)	14(4)	9(3)	9(3)	6(3)
C5	18(4)	21(4)	25(5)	12(4)	8(4)	2(4)
C6	16(4)	21(4)	20(4)	13(4)	8(3)	3(3)
N1	29(5)	36(5)	32(5)	16(4)	13(4)	20(4)
N2	22(4)	29(4)	16(4)	11(3)	4(3)	9(3)
N3	23(4)	33(5)	25(4)	18(4)	6(3)	14(4)
N4	25(4)	26(4)	23(4)	12(3)	5(3)	8(3)
N5	26(4)	32(5)	21(4)	13(4)	11(4)	12(4)
N6	24(4)	30(4)	18(4)	16(4)	7(3)	14(3)
N7	22(4)	26(4)	15(3)	11(3)	4(3)	10(3)
N8	25(4)	24(4)	16(4)	12(3)	10(3)	11(3)

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