Synergism of [$C_2N_4H_7S$] Cation and Anionic Modulators: Tailoring Second-Order Nonlinear Optics and Birefringence in Organic-Inorganic Crystals

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A. EXPERIMENTS AND CALCULATIONS

Synthesis. $(C_2N_4H_7S)SO_3NH_2$ single crystals were synthesized by slow evaporation from an aqueous solution. Amidinothiourea (0.01 mol, 1.18 g) and aminosulfonic acid (0.01 mol, 0.97 g) were dissolved in 20 ml of deionized water and stirred thoroughly at 40 °C for 3 h. After a few days, colorless needle-like crystals were successfully obtained.

The reagents were. Amidinothiourea (0.005 mol, 0.5908 g) and 1 ml of tetrafluoroboric acid were dissolved in 20 ml of anhydrous ethanol and stirred thoroughly at 40 °C for 3 h. After a few days, $(C_2N_4H_7S)BF_4$ colorless massive crystals were successfully obtained.

Structural Characterizations. The single-crystal XRD data were collected on a Bruker D8 VENTURE diffractometer equipped with a PHOTON II detector and Mo IμS 3.0microfocus X-ray sources (λ = 0.71073 Å). The collected data were processed using the Olex2 software.[1, 2] Atomic positions and isotropic thermal parameters were refined using the least squares method according to $Fo^2 \geq 2\sigma\ (Fo^2)$. The structures were checked by the program PLATON2 and no higher symmetries were found. The crystallographic information is summarized in Table S1. The atomic coordinates and the anisotropic displacement parameters are available in Table S2 to S3. The selected bond lengths and angles are listed in Table S4.

Phase Analysis. Powder XRD data were measured on a Dandong Haoyuan DX-27mini X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). The powder XRD pattern was scanned over the 2θ angles range of 5-70 °, at a scanning step width of 0.02 ° and a fixed counting time of 2 s. EDX microanalysis of the crystal was recorded on a Hitachi TM4000Plus microscopes with the acceleration voltage of 15 kV. In addition, the elemental mapping images were recorded to show the distribution of chemical elements. The IR spectrum of $(C_2N_4H_7S)SO_3NH_2$ and$(C_2N_4H_7S)BF_4$ at room temperature was scanned with a Nicolet iS10 spectrometer in the wavelength of 400-4000 cm-1 by potassium bromide tablet pressing method. The IR spectrum of $(C_2N_4H_7S)BF_4$ at room temperature was scanned with a Nicolet iS10 spectrometer in the wavelength of 400-4000 cm^{-1} by potassium bromide tablet pressing method.

Ultraviolet−Visible diffuse reflectance Spectrum. The UV-Vis-NIR diffuse reflectance spectrum of $(C_2N_4H_7S)SO_3NH_2$ and $(C_2N_4H_7S)BF_4$ were recorded in a Shimadzu UV-2600i spectrometer in the wavelength range of 200-900 nm. The reflectance was converted into absorption using the Kubelka-Munk method:$(F(R)h\nu)^{1/n} = K/S=(1-R)^2/2R= B(h\nu\text{-}Eg)$ (K: absorption coefficient; S: reflectance coefficient; R:reflectivity (in percentage form); h: Planck's constant; ν: frequency).

Thermal Analysis. Thermogravimetric analysis (TGA) was collected using a NETZSCH STA449F3 thermal analyzer. The crystal samples were heated from 30 to 900 °C at a heating rate of 10 °C min^{-1}.

Birefringence Measurement. The birefringence was measured by interference color method3 using a NIKON Eclipse Ci-POL polarizing microscope equipped with Berek compensator calibrated at 546 nm. The birefringence index was calculated by the formula $R = \Delta n \times d$, where R, Δn and d are the optical path difference measured by polarizing microscope, the birefringence index and the crystal thickness were measured by single-crystal X-ray diffraction, respectively.

SHG responses. Powder SHG efficiency was measured on a Q-switched Nd: YAG laser with radiation at 1064 nm according to a modified method of Kurtz and Perry.[3, 4] KH_2PO_4 (KDP) samples in the same particle size ranges were applied as the standard.

Theoretical Calculations. The first-principles calculations on electronic structure, band structure, and optical properties of $(C_2N_4H_7S)SO_3NH_2$ and $(C_2N_4H_7S)BF_4$ were carried out by using the CASTEP software package. The generalized gradient approximation (GGA) was adopted, and Perdew-Burke-Ernzerhof (PBE)[5, 6] functional6 with norm-conserving pseudopotentials was chosen to calculate the exchange-correlation potential. The valences of composed atoms were H:1s^1, B:2$s^2$2p^1, C:2$s^2$2p^2, N:2$s^2$2p^3, O:2$s^2$2p^4, F:2$s^2$2p^5 and S:3$s^2$3p^4. The high kinetic energy cutoff was set as 750eV and dense 2 ×2 ×2 Monkhorst-Pack7 k-point meshes in the Brillouin zones were adopted. The energy change, maximum force, maximum stress, and maximum displacement in the optimization were set as 1×10−6 eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively. The calculations on polarizability anisotropy were conducted using the DFT method, as implemented in the Gaussian09 package8 at the B3LYP/6-311G level.

B. Supporting Figures

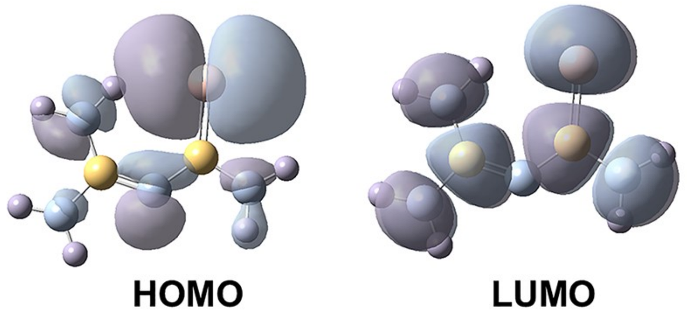

Figure S1. HOMO-LUMO map of [$C_2N_4H_7S$].

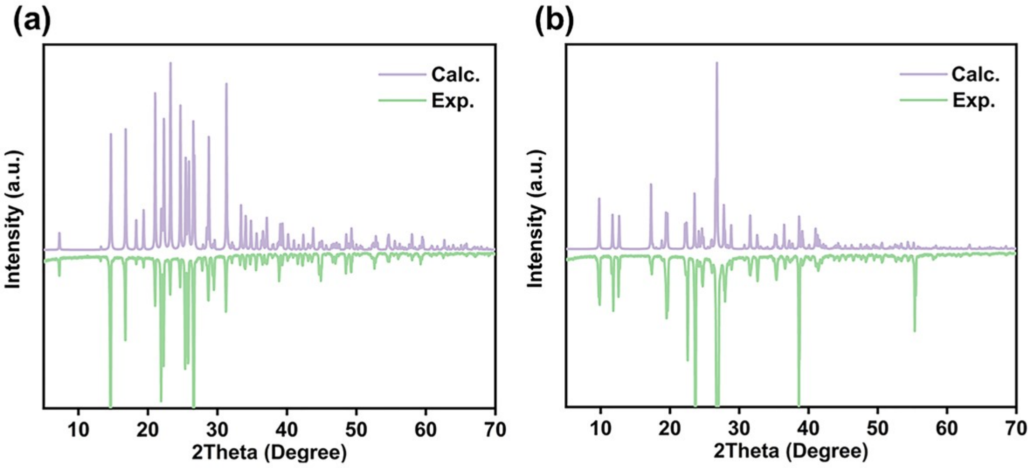

Figure S2. The powder X-ray diffraction for (a) $(C_2N_4H_7S)SO_3NH_2$ and (b) $(C_2N_4H_7S)BF_4$.

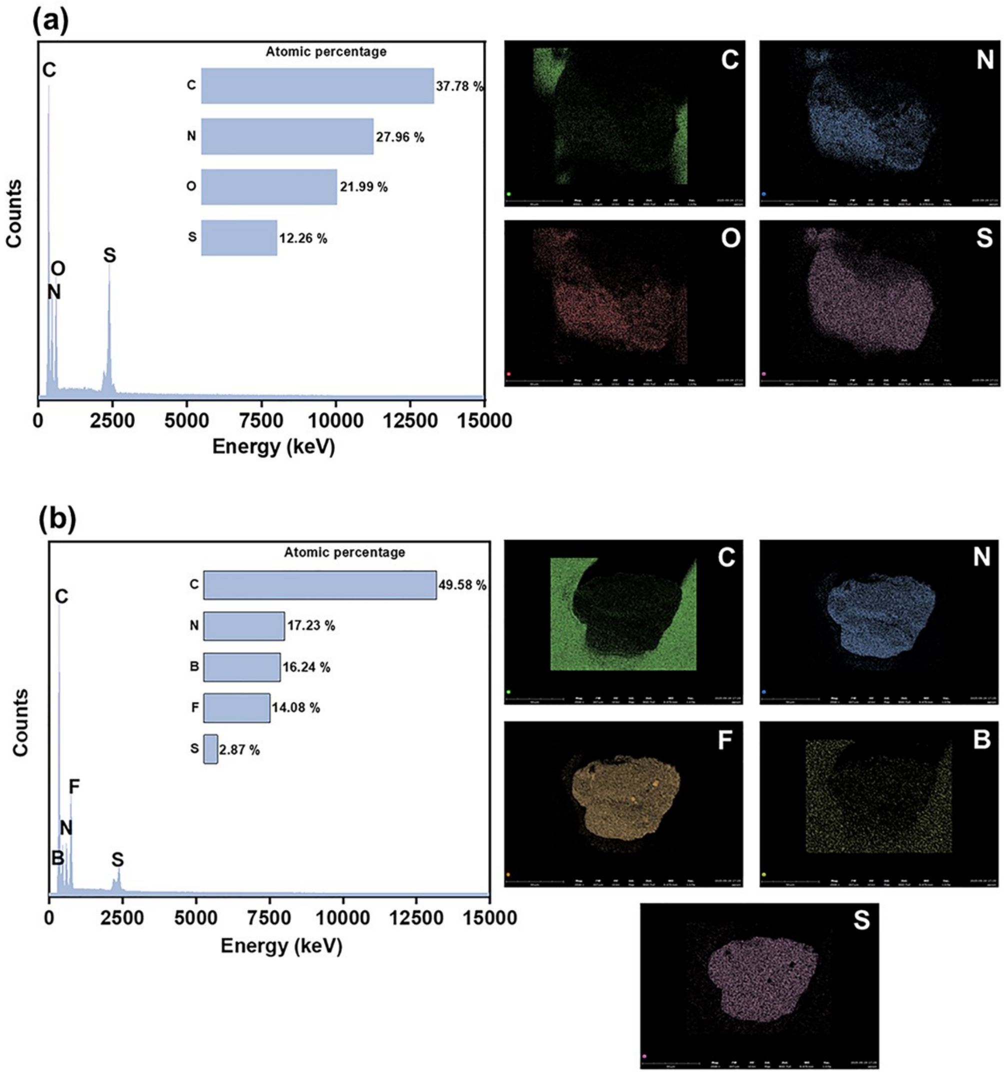

Figure S3. The energy-dispersive X-ray spectroscopy (EDS) element analysis of (a) $(C_2N_4H_7S)SO_3NH_2$ and (b) $(C_2N_4H_7S)BF_4$.

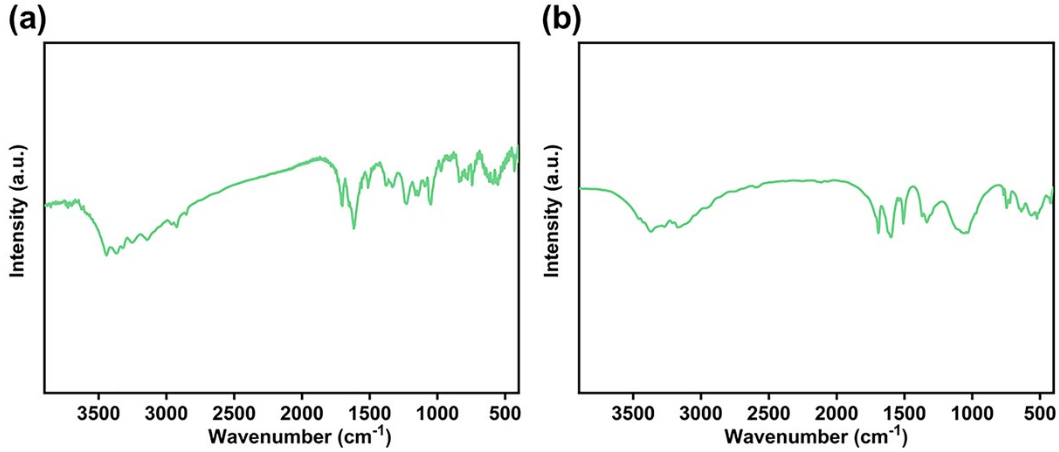

Figure S4. The IR spectra of (a) $(C_2N_4H_7S)SO_3NH_2$ and (b) $(C_2N_4H_7S)BF_4$.

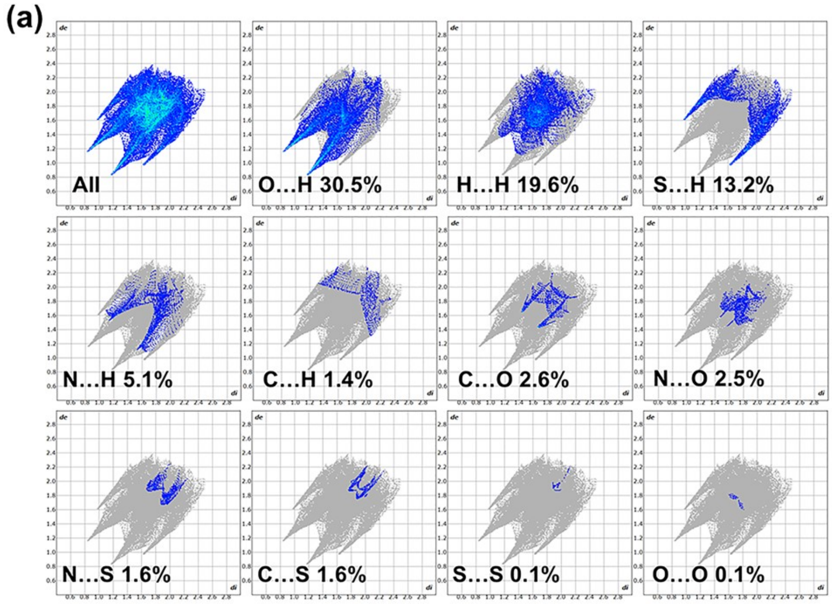

Figure S5. 2D fingerprint plots for individual interactions of atom types in crystal packing of $(C_2N_4H_7S)SO_3NH_2$.

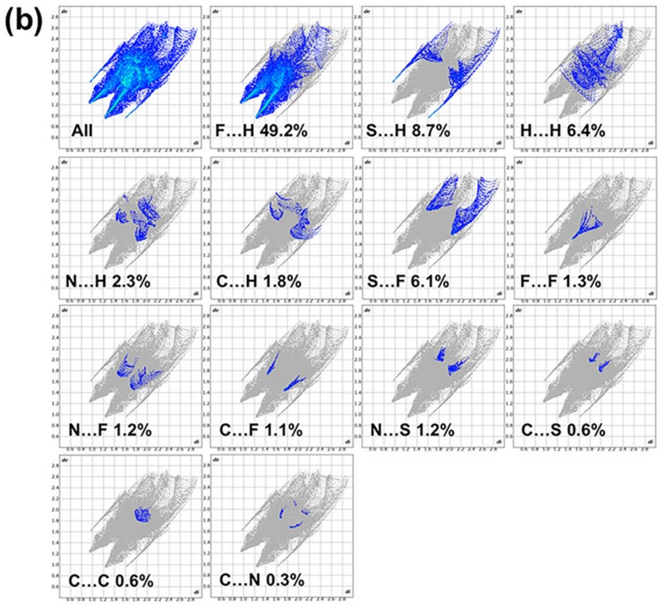

Figure S6. 2D fingerprint plots for individual interactions of atom types in crystal packing of $(C_2N_4H_7S)BF_4$.

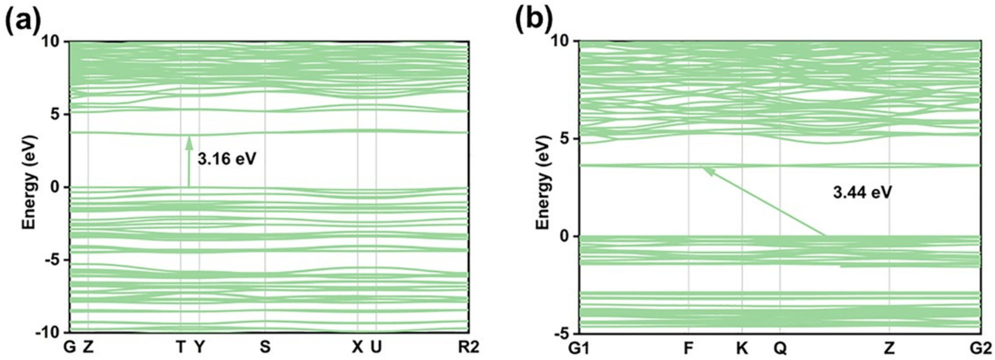

Figure S7. The calculated band structures of (a) $(C_2N_4H_7S)SO_3NH_2$ and (b) $(C_2N_4H_7S)BF_4$.

C. Supporting Tables

Table S1. Crystallographic information for $(C_2N_4H_7S)SO_3NH_2$ and $(C_2N_4H_7S)BF_4$.

Empirical formula	**$(C_2N_4H_7S)SO_3NH_2$**	**$(C_2N_4H_7S)BF_4$**
Formula weight	215.26	205.99
Temperature [K]	301(2)	301(2)
Crystal system	orthorhombic	triclinic
Space group (number)	$P2_12_12_1$ (19)	$P\bar{1}$ (2)
a [Å]	4.940(2)	5.6916(4)
b [Å]	6.946(3)	8.2102(5)
c [Å]	24.305(12)	9.5356(7)
α [°]	90	107.538(3)
β [°]	90	91.200(3)
γ [°]	90	104.227(3)
Volume [Å^3]	834.0(7)	409.67(5)
Z	4	2
ρ_{calc} [gcm^{-3}]	1.714	1.670
μ [mm^{-1}]	0.618	0.415
F(000)	448	208
Index ranges	$-6 \leq h \leq 6$ $-8 \leq k \leq 8$ $-31 \leq l \leq 31$	$-7 \leq h \leq 7$ $-10 \leq k \leq 10$ $-12 \leq l \leq 12$
Reflections collected	4283	25075
Independent reflections	1852 R_{int} = 0.0474 R_{sigma} = 0.0661	1890 R_{int} = 0.0574 R_{sigma} = 0.0229
Completeness to theta	99.8 %	100.0 %
Data / Restraints / Parameters	1852 / 2 / 115	1890 / 0 / 110
Goodness-of-fit on F^2	1.037	1.029
R/wR (I>2 σ(I)) [a]	R_1 = 0.0475 wR_2 = 0.0845	R_1 = 0.0389 wR_2 = 0.0760
R/wR (all data) [a]	R_1 = 0.0738 wR_2 = 0.0953	R_1 = 0.0603 wR_2 = 0.0863
Largest peak/hole [eÅ^{-3}]	0.32/−0.35	0.24/−0.19
Flack X parameter	0.07(11)	/

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

Table S2. Atomic coordinates and U_{eq} [Å^2] for $(C_2N_4H_7S)SO_3NH_2$.

Atom	***x***	***y***	***z***	***U*****eq**
S2	0.0931(2)	−0.16531(18)	0.31581(5)	0.0324(3)
S1	0.2464(3)	0.04929(19)	0.48538(6)	0.0407(4)
N1	0.6232(9)	−0.1562(6)	0.43742(17)	0.0432(11)
H1A	0.747955	−0.171786	0.413155	0.052
H1B	0.588036	−0.246589	0.460510	0.052
N2	0.5722(8)	0.1337(5)	0.39875(15)	0.0297(9)
H2	0.716778	0.100649	0.381451	0.036
N3	0.2579(9)	0.3839(5)	0.40843(17)	0.0385(10)
H3A	0.193928	0.491820	0.396937	0.046
H3B	0.188521	0.329159	0.436858	0.046
N4	0.5686(9)	0.3860(6)	0.33902(17)	0.0426(11)
H4A	0.505551	0.493901	0.327321	0.051
H4B	0.701919	0.332131	0.322274	0.051
N5	−0.0678(10)	−0.1862(7)	0.25755(19)	0.0435(11)
H5A	−0.036(12)	−0.299(5)	0.247(2)	0.052
H5B	−0.236(5)	−0.175(8)	0.261(2)	0.052
C1	0.4608(10)	0.3031(7)	0.38267(19)	0.0300(11)
C2	0.4863(10)	0.0058(7)	0.4392(2)	0.0300(11)
O1	0.3737(7)	−0.1972(6)	0.30274(17)	0.0573(12)
O2	0.0295(7)	0.0289(5)	0.33317(14)	0.0408(9)
O3	−0.0080(7)	−0.3047(5)	0.35579(15)	0.0461(10)

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

Table S3. Atomic coordinates and U_{eq} [Å^2] for $(C_2N_4H_7S)BF_4$.

Atom	***x***	***y***	***z***	***U***
S1	0.34638(11)	0.72499(8)	0.07465(7)	0.0540(2)
F1	−0.3492(2)	0.12594(17)	0.43574(15)	0.0606(4)
F2	−0.5498(3)	0.2039(2)	0.2718(2)	0.0896(6)
F3	−0.1474(3)	0.2284(2)	0.2681(2)	0.0906(6)
F4	−0.2850(3)	0.41399(18)	0.44998(19)	0.0880(5)
N1	0.0044(3)	0.9019(2)	0.2555(2)	0.0574(5)
H1A	−0.059706	0.989552	0.283911	0.069
H1B	0.115332	0.903806	0.195683	0.069
N2	−0.2356(3)	0.7611(2)	0.3941(2)	0.0526(5)
H2A	−0.301615	0.847543	0.423686	0.063
H2B	−0.280336	0.670538	0.424367	0.063
N3	0.0314(3)	0.6267(2)	0.26179(18)	0.0411(4)
H3	−0.026639	0.544913	0.300271	0.049
N4	0.2629(3)	0.4444(2)	0.1607(2)	0.0548(5)
H4A	0.189488	0.379503	0.210856	0.066
H4B	0.371309	0.411667	0.105511	0.066
C1	−0.0662(3)	0.7673(2)	0.3026(2)	0.0396(4)
C2	0.2093(3)	0.5935(2)	0.1683(2)	0.0379(4)
B1	−0.3358(4)	0.2417(3)	0.3550(3)	0.0447(6)

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

Table S4. Hydrogen bonds for $(C_2N_4H_7S)SO_3NH_2$.

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N1–H1A···S2#1	0.86	2.92	3.759(5)	166.8
N1–H1A···O3#1	0.86	2.06	2.885(6)	160.0
N1–H1B···S1#2	0.86	2.60	3.369(4)	149.3
N4–H4A···O1#3	0.86	2.32	3.176(6)	173.0
N4–H4B···N5#4	0.86	2.65	3.441(6)	152.7
N3–H3A···O3#3	0.86	2.00	2.836(5)	164.2
N3–H3B···S1	0.86	2.29	2.984(4)	137.6
N3–H3B···S1#5	0.86	3.01	3.642(5)	132.0
N2–H2···O2#1	0.86	2.00	2.859(5)	173.4
N5–H5A···S2#6	0.84(2)	2.98(3)	3.777(5)	160(5)
N5–H5A···O2#6	0.84(2)	2.28(4)	2.969(6)	140(5)
N5–H5B···O1#7	0.84(2)	2.18(3)	2.971(6)	157(5)

Symmetry transformations used to generate equivalent atoms:

#1: 1+X, +Y, +Z; #2: 0.5+X, -0.5-Y, 1-Z; #3: +X, 1+Y, +Z; #4: 1-X, 0.5+Y, 0.5-Z; #5: -0.5+X, 0.5-Y, 1-Z; #6: -X, -0.5+Y, 0.5-Z; #7: -1+X, +Y, +Z;

Table S5. Hydrogen bonds for $(C_2N_4H_7S)BF_4$.

D–H···A [Å]	**d(D–H) [Å]**	**d(H···A) [Å]**	**d(D···A) [Å]**	**<(DHA) [°]**
N1–H1A···F1#1	0.86	2.47	3.232(2)	148.3
N1–H1A···F3#1	0.86	2.19	2.982(2)	154.1
N1–H1B···S1	0.86	2.28	2.9822(18)	138.6
N1–H1B···F2#2	0.86	2.61	3.045(2)	112.9
N2–H2A···F1#1	0.86	2.34	3.130(2)	153.6
N2–H2A···F1#3	0.86	2.44	3.067(2)	130.5
N2–H2B···F4	0.86	2.19	3.002(2)	158.2
N3–H3···F3	0.86	2.44	3.197(2)	147.2
N3–H3···F4	0.86	2.36	3.161(2)	154.2
N4–H4A···F2#4	0.86	2.48	2.899(2)	111.0
N4–H4A···F3	0.86	2.19	2.967(2)	150.2
N4–H4B···S1#5	0.86	2.58	3.4298(18)	172.5

Symmetry transformations used to generate equivalent atoms:

#1: +X, 1+Y, +Z; #2: 1+X, 1+Y, +Z; #3: -1-X, 1-Y, 1-Z; #4: 1+X, +Y, +Z; #5: 1-X, 1-Y, -Z;

Table S6. Bond lengths [Å] and angles [°] for $(C_2N_4H_7S)SO_3NH_2$.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
S2–O1	1.439(4)	O1–S2–O2	114.6(2)
S2–O2	1.448(4)	O1–S2–O3	112.0(3)
S2–O3	1.460(4)	O2–S2–O3	110.5(2)
S2–N5	1.631(5)	O1–S2–N5	105.3(3)
S1–C2	1.660(5)	O2–S2–N5	103.3(2)
N1–C2	1.313(6)	O3–S2–N5	110.6(2)
N1–H1A	0.8600	C2–N1–H1A	120.0
N1–H1B	0.8600	C2–N1–H1B	120.0
N2–C1	1.357(6)	H1A–N1–H1B	120.0
N2–C2	1.392(6)	C1–N2–C2	129.3(4)
N2–H2	0.8600	C1–N2–H2	115.3
N3–C1	1.308(6)	C2–N2–H2	115.3
N3–H3A	0.8600	C1–N3–H3A	120.0
N3–H3B	0.8600	C1–N3–H3B	120.0
N4–C1	1.319(6)	H3A–N3–H3B	120.0
N4–H4A	0.8600	C1–N4–H4A	120.0
N4–H4B	0.8600	C1–N4–H4B	120.0
N5–H5A	0.84(2)	H4A–N4–H4B	120.0
N5–H5B	0.84(2)	S2–N5–H5A	105(4)
		S2–N5–H5B	112(4)
		H5A–N5–H5B	108(6)
		N3–C1–N4	120.5(4)
		N3–C1–N2	123.0(4)
		N4–C1–N2	116.5(4)
		N1–C2–N2	111.5(4)
		N1–C2–S1	123.1(4)
		N2–C2–S1	125.4(4)

Table S7. Bond lengths [Å] and angles [°] for $(C_2N_4H_7S)BF_4$.

Atom–Atom	**Length [Å]**	**Atom–Atom–Atom**	**Angle [°]**
S1–C2	1.6635(19)	C1–N1–H1A	120.0
F1–B1	1.381(2)	C1–N1–H1B	120.0
F2–B1	1.355(3)	H1A–N1–H1B	120.0
F3–B1	1.374(3)	C1–N2–H2A	120.0
F4–B1	1.386(3)	C1–N2–H2B	120.0
N1–C1	1.294(2)	H2A–N2–H2B	120.0
N1–H1A	0.8600	C1–N3–C2	130.59(16)
N1–H1B	0.8600	C1–N3–H3	114.7
N2–C1	1.316(2)	C2–N3–H3	114.7
N2–H2A	0.8600	C2–N4–H4A	120.0
N2–H2B	0.8600	C2–N4–H4B	120.0
N3–C1	1.358(2)	H4A–N4–H4B	120.0
N3–C2	1.386(2)	N1–C1–N2	121.22(18)
N3–H3	0.8600	N1–C1–N3	122.05(18)
N4–C2	1.315(2)	N2–C1–N3	116.73(17)
N4–H4A	0.8600	N4–C2–N3	112.74(17)
N4–H4B	0.8600	N4–C2–S1	122.14(15)
		N3–C2–S1	125.11(14)
		F2–B1–F3	111.1(2)
		F2–B1–F1	110.36(18)
		F3–B1–F1	108.40(17)
		F2–B1–F4	109.05(18)
		F3–B1–F4	108.10(19)
		F1–B1–F4	109.8(2)

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