Supplementary information

H/F Substitution Strategy Can Achieve Large Spontaneous Polarization in 1D Hybrid Perovskite Ferroelectric

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Experimental Section

Synthesis and Growth of Crystals

All chemical reagents used in this work were obtained from commercial sources without further purification. The synthesis of the ligands BTAB and 3-F-BTAB can refer to previous reports. Weigh 2 mmol of BTAB in a beaker, dissolve with hydrobromic acid, and then add 2mmol of $PbBr_2$. After complete dissolution, slowly evaporate the solution at room temperature, and after a few weeks, a colorless block crystal of (BTAB)$PbBr_3$ was obtained. Crystal of (3-F-BTAB)$PbBr_3$ was obtained in the same way.

Detailed methods of measurements

Variable-Temperature Single-crystal XRD

The Rigaku Saturn 724 diffractometer with Mo Kα radiation (λ = 0.71073 Å) was used to obtain single crystal X-ray diffraction data. The direct method was used to solve the variable temperature crystal structure data, and the SHELXL software was used to analyze and refine the crystal structure. Import the generated CIF file into DIAMOND to draw the corresponding asymmetric cell diagram and stack diagram, and calculate the selected bond distances and angles through Mercury. Table S1-S3 summarize the data collection of these crystals. These X-ray crystal structures have been stored at the Cambridge Crystallography Data Center (storage number CCDC 2350277, 2350294-2350295) and are available free of charge from CCDC at www.ccdc.cam.ac.uk/getstructures.

DSC Measurement

Grind crystal into powder, weigh about 10 mg of powder, and place it in an aluminum crucible. Under nitrogen protection of the environment, the NETZSCH DSC 214 Polymer instrument is used to uniformly heat and cool at a rate of 30 K min^{-1} in the temperature range of 233 to 435 K.

Dielectric Measurement

Press the powder sample into sheets, use conductive silver glue and copper wire as the medium, and connect the sheet sample to both ends of the electrode to make a capacitor. The complex dielectric constant at different frequencies in the temperature range of 330~440 K was measured using Tonghui TH2828A instrument at 1V AC voltage.

SHG Measurement

Temperature-varying SHG experiments were performed by using a low-divergence unexpanded laser beam in the temperature range of 330-450 K, which pulsed in Nd: YAG. (The wavelength is 1064 nm, the peak power is 1.6 MW, the repetition rate is 10 Hz, and the pulse duration is 5 ns).

UV-visible (UV-vis) Spectrophotometry

UV-vis absorption spectra of these compounds were characterized using a Shimadzu UV-2600 spectrophotometry equipped with a xenon lamp as the excitation source at room temperature.

Density Functional Theory (DFT) Calculations

The band structure, partial density state and ferroelectric polarization calculation were performed based on density function theory (DFT) by using the Vienna Ab-initio Simulation Package (VASP).[1] The crystallographic structures of (3-F-BTAB)$PbBr_3$ obtained from SC-XRD measurement were further optimized geometrically, employing the exchange-correlation interactions within the generalized gradient approximation (GGA) on the basis of the PerdewBurke-Ernzerh (PBE) function.[2]

The band structure and partial density state of optimized structures were calculated by the PBE function with considering spin-orbit coupling (SOC). Meanwhile, the plane wave cut-off energy, the force and energy convergence criterions were set to be 500 eV, 0.015 eV/Å and 10^{-5} eV per atom, respectively, and the mesh samplings in the Brillouin zone were 3 × 2 × 1 for (3-F-BTAB)$PbBr_3$. In addition, the other parameters and convergent criteria were the default values. Finally, the post-processing analysis was performed by using VASPKIT.

Ferroelectric polarization calculation was based on the Berry phase method developed by Kingsmith and Vanderbilt.[3] The calculation was based on the crystal structures of (3-F-BTAB)$PbBr_3$, and 2 × 2 × 4 k-point meshed were used. The cut-off energy was set as 500 eV for the system.

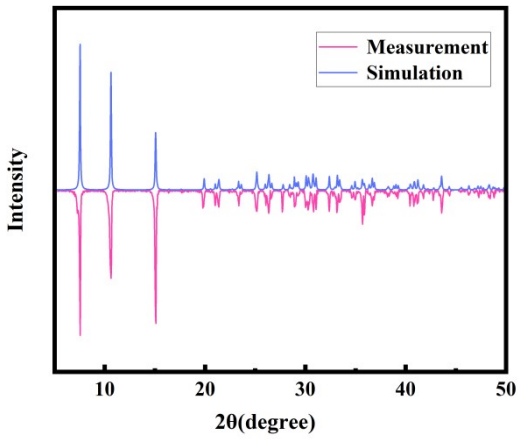

Fig. S1 The measured and simulated PXRD patterns of (3-F-BTAB)$PbBr_3$ match well, verifying the phase purity of (3-F-BTAB)$PbBr_3$.

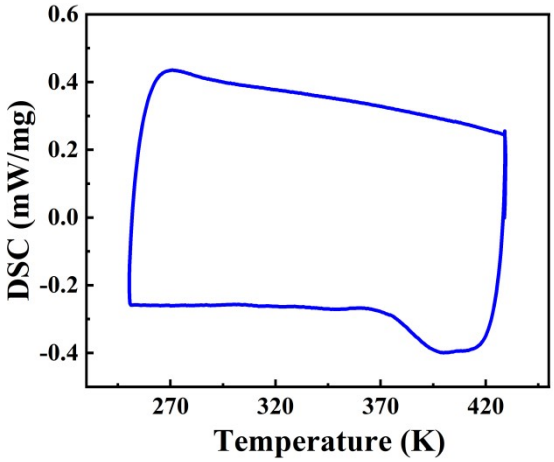

Fig. S2 DSC curves of (BTAB)$PbBr_3$ in the heating-cooling cycle.

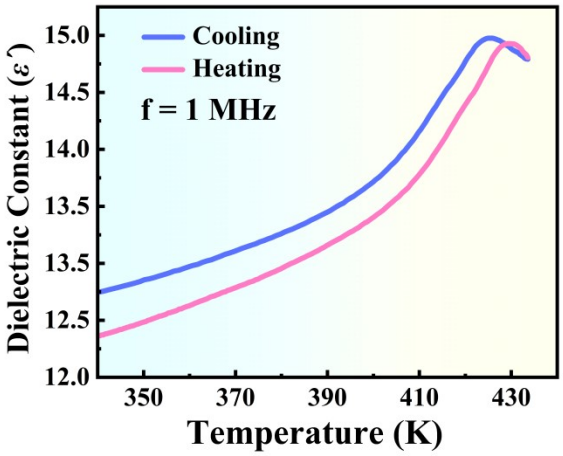

Fig. S3 Dielectric constant (ε') of (3-F-BTAB)$PbBr_3$ as a function of temperature at 1 MHz.

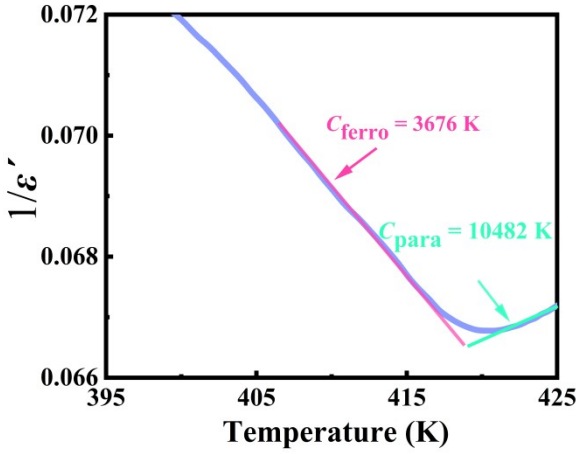

Fig. S4 $1/\varepsilon'$ of (3-F-BTAB)$PbBr_3$ as a function of temperature at 1 MHz.

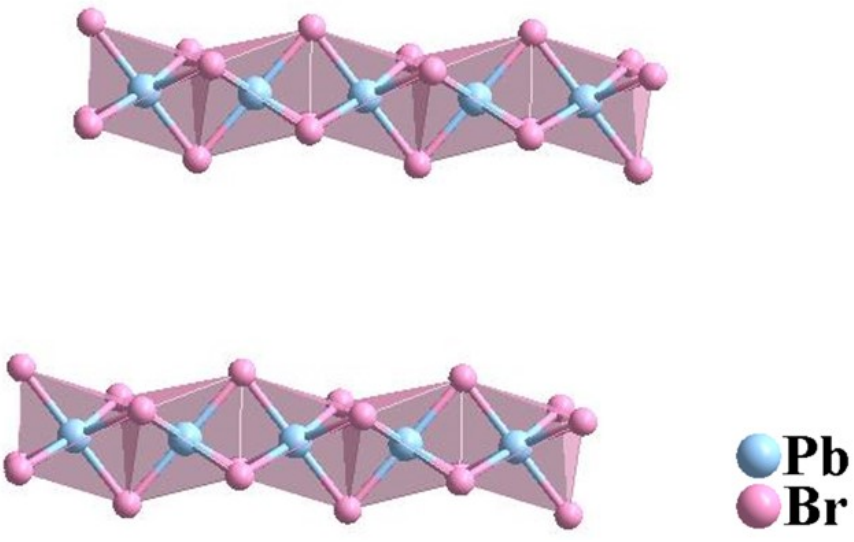

Fig. S5 The face-sharing $[PbBr_3]^-$ infinite 1D anionic chains in (3-F-BTAB)$PbBr_3$.

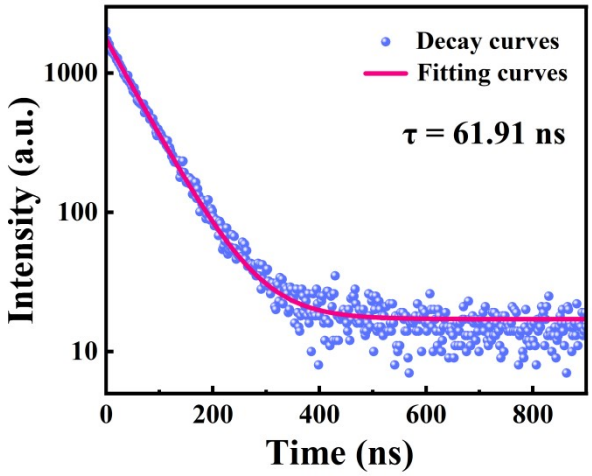

Fig. S6 Decay curves and calculated PL lifetimes of (3-F-BTAB)$PbBr_3$.

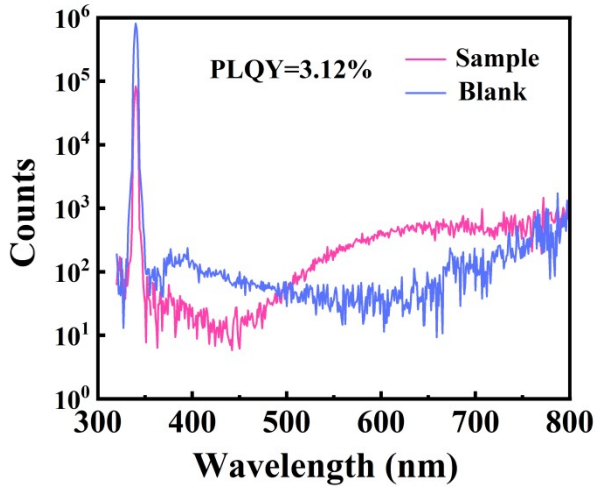

Fig. S7 Quantum yield of (3-F-BTAB)$PbBr_3$.

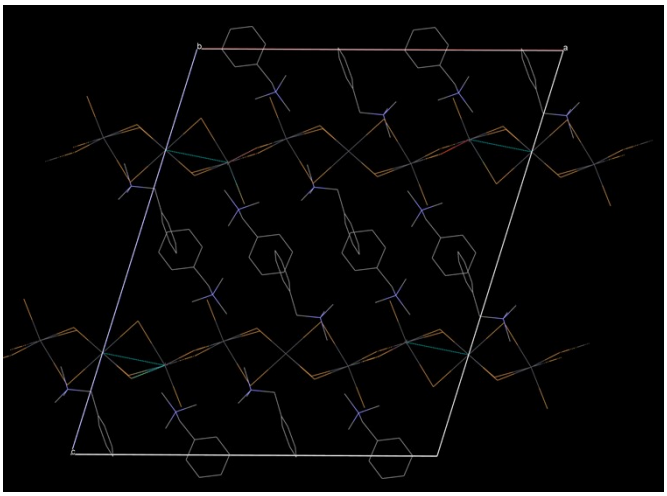

Fig.S8 Packing diagram of (BTAB)$PbBr_3$ and schematic diagram of intermolecular interactions.

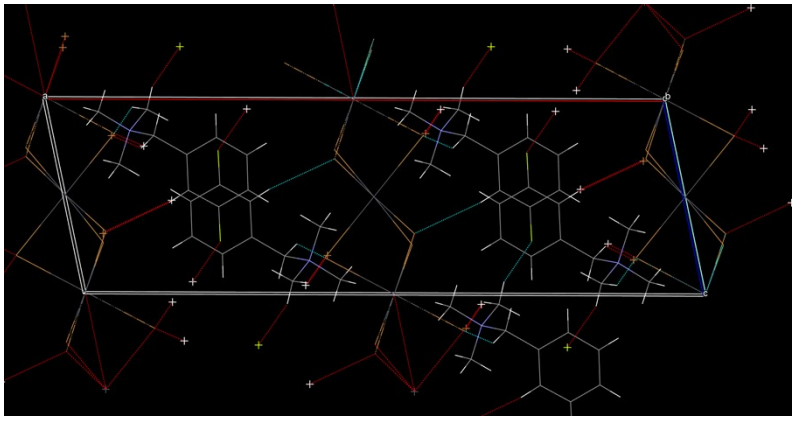

Fig.S9 Packing diagram of (3-F-BTAB)$PbBr_3$ and schematic diagram of intermolecular interactions.

Table S1 Crystal data and structure refinements for (BTAB)$PbBr_3$ and (3-F-BTAB)$PbBr_3$ at 273 K and 420 K.

	(BTAB)$PbBr_3$ (293 K)	**(3-F-BTAB)$PbBr_3$ (273 K)**	**(3-F-BTAB)$PbBr_3$ (420 K)**
Empirical formula	$C_{20}Br_5N_2Pb_{1.50}$	$C_{10}H_{15}Br_3FNPb$	$C_{10}H_{15}Br_3FNPb$
Formula weight	978.56	615.15	615.15
Space group	*C*2/*c* (15)	*C*2 (5)	*C*2/*c* (15)
Crystal system	monoclinic	monoclinic	monoclinic
a/ Å	23.110(3)	23.977(5)	23.5064(18)
b/ Å	9.6090(13)	8.9117(16)	8.9668(5)
c/ Å	26.851(4)	7.7036(15)	6.8118(4)
α/°	90	90	90
β/°	106.990(14)	101.973(5)	98.299(7)
γ/°	90	90	90
Volume/ Å^3	5702.4(13)	1610.2(5)	1420.74(16)
Z	8	4	4
F(000)	3456	1112	1112
GOF	1.033	0.979	0.993
R_{int}	0.1032	0.0794	0.0219
R_1	0.0648	0.0388	0.0845
wR_2	0.1280	0.0678	0.2630

Table S2 The bond lengths (Å) and angles (º) of (3-F-BTAB)$PbBr_3$ in the LTP.

Atom–Atom	**Length [Å]**	**Atom–Atom–Atom**	**Angle [°]**
Pb2–Br3	3.0276(7)	Br3–Pb2–Br3	178.29(4)
Pb2–Br3^1	3.0276(7)	Br3–Pb2–Br1	99.55(3)
Pb2–Br2	2.9241(10)	Br3–Pb2–Br1	99.55(3)
Pb2–Br2^1	2.9241(10)	Br3–Pb2–Br1	81.59(2)
Pb2–Br1^1	3.1549(10)	Br3–Pb2–Br1	81.60(2)
Pb2–Br1	3.1549(10)	Br2–Pb2–Br3	86.27(3)
Pb1–Br3^2	3.0310(7)	Br2–Pb2–Br3	92.54(2)
Pb1–Br3	3.0309(7)	Br2–Pb2–Br3	86.28(3)
Pb1–Br2^2	3.1875(10)	Br2–Pb2–Br3	92.54(3)
Pb1–Br2	3.1875(10)	Br2–Pb2–Br2	92.64(4)
Pb1–Br1	2.9080(10)	Br2–Pb2–Br1	85.11(2)
Pb1–Br1^2	2.9081(10)	Br2–Pb2–Br1	173.83(2)
N1–C4	1.523(9)	Br2–Pb2–Br1	173.83(2)
N1–C3	1.490(10)	Br2–Pb2–Br1	85.11(2)
N1–C2	1.501(9)	Br1–Pb2–Br1	97.69(4)

N1–C1	1.492(10)	Br3–Pb1–Br3	177.37(4)
F1–C9	1.371(12)	Br3–Pb1–Br2	96.57(3)
C4–H4A	0.9700	Br3–Pb1–Br2	81.73(2)
C4–H4B	0.9700	Br3–Pb1–Br2	81.73(2)
C4–C5	1.498(11)	Br3–Pb1–Br2	96.57(3)
C6–H6	0.9300	Br2–Pb1–Br2	100.24(4)
C6–C7	1.383(12)	Br1–Pb1–Br3	85.72(3)
C6–C5	1.376(10)	Br1–Pb1–Br3	85.72(3)
C7–H7	0.9300	Br1–Pb1–Br3	96.14(3)
C7–C8	1.366(14)	Br1–Pb1–Br3	96.14(3)
C5–C10	1.401(12)	Br1–Pb1–Br2	84.79(3)
C10–H10	0.9300	Br1–Pb1–Br2	174.71(3)
C10–C9	1.356(13)	Br1–Pb1–Br2	84.79(3)
C3–H3A	0.9600	Br1–Pb1–Br2	174.71(3)
C3–H3B	0.9600	Br1–Pb1–Br1	90.24(4)
C3–H3C	0.9600	Pb2–Br3–Pb1	78.96(2)
C2–H2A	0.9600	Pb2–Br2–Pb1	78.01(3)
C2–H2B	0.9600	Pb1–Br1–Pb2	78.77(3)
C2–H2C	0.9600	C3–N1–C4	110.8(6)
C1–H1A	0.9600	C3–N1–C2	108.3(7)
C1–H1B	0.9600	C3–N1–C1	108.5(7)
C1–H1C	0.9600	C2–N1–C4	108.2(6)
C9–C8	1.366(14)	C1–N1–C4	111.6(7)
C8–H8	0.9300	C1–N1–C2	109.4(7)
		N1–C4–H4A	108.3
		N1–C4–H4B	108.3
		H4A–C4–H4B	107.4
		C5–C4–N1	115.8(6)
		C5–C4–H4A	108.3
		C5–C4–H4B	108.3
		C7–C6–H6	119.3
		C5–C6–H6	119.3
		C5–C6–C7	121.4(9)
		C6–C7–H7	120.2
		C8–C7–C6	119.6(8)
		C8–C7–H7	120.2
		C6–C5–C4	122.0(8)
		C6–C5–C10	118.7(8)
		C10–C5–C4	119.3(7)
		C5–C10–H10	120.9
		C9–C10–C5	118.3(8)
		C9–C10–H10	120.9
		N1–C3–H3A	109.5
		N1–C3–H3B	109.5
		N1–C3–H3C	109.5
		H3A–C3–H3B	109.5
		H3A–C3–H3C	109.5
		H3B–C3–H3C	109.5
		N1–C2–H2A	109.5
		N1–C2–H2B	109.5
		N1–C2–H2C	109.5
		H2A–C2–H2B	109.5
		H2A–C2–H2C	109.5
		H2B–C2–H2C	109.5
		N1–C1–H1A	109.5
		N1–C1–H1B	109.5
		N1–C1–H1C	109.5

		H1A–C1–H1B	109.5
		H1A–C1–H1C	109.5
		H1B–C1–H1C	109.5
		C10–C9–F1	118.0(9)
		C10–C9–C8	123.4(9)
		C8–C9–F1	118.5(9)
		C7–C8–H8	120.7
		C9–C8–C7	118.7(8)
		C9–C8–H8	120.7

Symmetry codes: [1] :1-X, +Y, 1-Z; [2] :1-X, +Y, 2-Z.

Table S3. The bond lengths (Å) and angles (º) of (3-F-BTAB)$PbBr_3$ in the HTP.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Pb1–Pb1[#1]	3.4059(2)	Pb1–Pb1–Pb1	179.97(5)
Pb1–Pb1[#2]	3.40590(19)	Br1–Pb1–Pb1	130.22(11)
Pb1–Br1	2.637(5)	Br1–Pb1–Pb1	49.78(11)
Pb1–Br2	2.616(4)	Br1–Pb1–Br3	82.63(14)
Pb1–Br3	2.690(4)	Br2–Pb1–Pb1	49.39(10)
N1–C4	1.501(9)	Br2–Pb1–Pb1	130.63(10)
N1–C2	1.501(9)	Br2–Pb1–Br1	83.81(15)
N1–C3	1.502(9)	Br2–Pb1–Br3	82.62(18)
N1–C1	1.500(9)	Br3–Pb1–Pb1	50.65(9)
C4–H4A	0.9700	Br3–Pb1–Pb1	129.33(10)
C4–H4B	0.9700	C4–N1–C2	109.3(10)
C4–C5	1.45(5)	C4–N1–C3	109.1(10)
C2–H2A	0.9599	C2–N1–C3	109.6(10)
C2–H2B	0.9594	C1–N1–C4	109.8(10)
C2–H2C	0.9601	C1–N1–C2	109.6(10)
C3–H3A	0.9600	C1–N1–C3	109.4(10)
C3–H3B	0.9600	N1–C4–H4A	108.8
C3–H3C	0.9601	N1–C4–H4B	108.8
C14–H14A	0.9700	H4A–C4–H4B	107.7
C14–H14B	0.9700	C5–C4–N1	114(2)
C14–C15	1.510(10)	C5–C4–H4A	108.8
C14–N2	1.498(9)	C5–C4–H4B	108.8
F1–C7	1.359(17)	N1–C2–H2A	110.1
C7–C6	1.3900	N1–C2–H2B	107.4
C7–C8	1.3900	N1–C2–H2C	110.9
C6–H6	0.9300	H2A–C2–H2B	109.5
C6–C5	1.3900	H2A–C2–H2C	109.5
C5–C10	1.3900	H2B–C2–H2C	109.5
C10–H10	0.9300	N1–C3–H3A	108.2
C10–C9	1.3900	N1–C3–H3B	108.7
C9–H9	0.9300	N1–C3–H3C	111.5
C9–C8	1.3900	H3A–C3–H3B	109.5
C8–H8	0.9300	H3A–C3–H3C	109.5
F2–C17	1.352(17)	H3B–C3–H3C	109.5
C16–H16	0.9300	H14A–C14–H14B	108.2
C16–C15	1.3900	C15–C14–H14A	109.7
C16–C17	1.3900	C15–C14–H14B	109.7
C15–C20	1.3900	N2–C14–H14A	109.7
C20–H20	0.9300	N2–C14–H14B	109.7
C20–C19	1.3900	N2–C14–C15	109.7(9)
C19–H19	0.9300	F1–C7–C6	120(2)
C19–C18	1.3900	F1–C7–C8	120(2)
Pb1–Pb1[#1]	3.4059(2)	C6–C7–C8	120.0

Pb1–Pb1$^{\#2}$	3.40590(19)	C7–C6–H6	120.0
Pb1–Br1	2.637(5)	C7–C6–C5	120.0
Pb1–Br2	2.616(4)	C5–C6–H6	120.0
Pb1–Br3	2.690(4)	C6–C5–C4	119.8(8)
N1–C4	1.501(9)	C6–C5–C10	120.0
N1–C2	1.501(9)	C10–C5–C4	120.2(8)
N1–C3	1.502(9)	C5–C10–H10	120.0
N1–C1	1.500(9)	C5–C10–C9	120.0
C4–H4A	0.9700	C9–C10–H10	120.0
C4–H4B	0.9700	C10–C9–H9	120.0
C4–C5	1.45(5)	C8–C9–C10	120.0
C2–H2A	0.9599	C8–C9–H9	120.0
C2–H2B	0.9594	C7–C8–H8	120.0
C2–H2C	0.9601	C9–C8–C7	120.0
C3–H3A	0.9600	C9–C8–H8	120.0
C3–H3B	0.9600	C15–C16–H16	120.0
C3–H3C	0.9601	C15–C16–C17	120.0
C14–H14A	0.9700	C17–C16–H16	120.0
C14–H14B	0.9700	C16–C15–C14	119.9(8)
C14–C15	1.510(10)	C20–C15–C14	120.1(8)
C14–N2	1.498(9)	C20–C15–C16	120.0
F1–C7	1.359(17)	C15–C20–H20	120.0
C7–C6	1.3900	C19–C20–C15	120.0
C7–C8	1.3900	C19–C20–H20	120.0
C6–H6	0.9300	C20–C19–H19	120.0
C6–C5	1.3900	C18–C19–C20	120.0
C5–C10	1.3900	C18–C19–H19	120.0
C10–H10	0.9300	C19–C18–H18	120.0
C10–C9	1.3900	C19–C18–C17	120.0
C9–H9	0.9300	C17–C18–H18	120.0
C9–C8	1.3900	F2–C17–C16	120(2)
C8–H8	0.9300	F2–C17–C18	120(2)
F2–C17	1.352(17)	C18–C17–C16	120.0
C16–H16	0.9300	C14–N2–C13	109.4(10)
C16–C15	1.3900	C14–N2–C11	109.7(10)
C16–C17	1.3900	C14–N2–C12	109.7(10)
C15–C20	1.3900	C13–N2–C11	109.2(10)
C20–H20	0.9300	C13–N2–C12	109.2(10)
C20–C19	1.3900	C11–N2–C12	109.6(10)
C19–H19	0.9300	N2–C13–H13A	108.3
C19–C18	1.3900	N2–C13–H13B	109.9
C18–H18	0.9300	N2–C13–H13C	110.2
C18–C17	1.3900	H13A–C13–H13B	109.5
N2–C13	1.500(9)	H13A–C13–H13C	109.5
N2–C11	1.501(9)	H13B–C13–H13C	109.5
N2–C12	1.501(9)	N2–C11–H11A	108.5
C13–H13A	0.9600	N2–C11–H11B	110.7
C13–H13B	0.9598	N2–C11–H11C	109.3
C13–H13C	0.9603	H11A–C11–H11B	109.5
C11–H11A	0.9601	H11A–C11–H11C	109.5
C11–H11B	0.9600	H11B–C11–H11C	109.5
C11–H11C	0.9600	N2–C12–H12A	110.0
C12–H12A	0.9600	N2–C12–H12B	109.9
C12–H12B	0.9601	N2–C12–H12C	108.6
C12–H12C	0.9601	H12A–C12–H12B	109.5
C1–H1A	0.9600	H12A–C12–H12C	109.5
C1–H1B	0.9600	H12B–C12–H12C	109.5

C1–H1C	0.9600	N1–C1–H1A	110.8
		N1–C1–H1B	109.0
		N1–C1–H1C	108.7
		H1A–C1–H1B	109.5
		H1A–C1–H1C	109.5
		H1B–C1–H1C	109.5

Symmetry codes: [1] :1-X, 1-Y, 1-Z; [2]: 1-X, 1-Y, -Z.

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