Supporting Information

Nicotinic acid bromide: a simple organic salt optical-electrical ferroelastic with high T_c

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Experimental Section

Synthesis

All chemical reagents are analytical grades without further purification. For three crystals, nicotinamide (10 mmol) and 5 mL inorganic acid (HX, X= Cl, Br, I) were mixed in distilled water (10 mL) at room temperature. The colorless single crystals were obtained by slow evaporation after a week. Another method was that the nicotinamide was replaced by nicotinic acid. At last, the three crystals were obtained with other same conditions. For three compounds, the elements C/N/O mass fractions were 0.45/0.088/0.20, 0.353/0.068/0.157, and 0.287/0.056/0.127, respectively.

Single crystal measurement

Single crystal data were measured by a Rigaku Saturn 724 X-ray diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 293 K and 413 K, respectively. The CCDC numbers are 2215497-2215500. Different temperatures structures were calculated by direct method and refined using full-matrix method with Olex2 software. Hydrogen atoms are added and refined geometrically. Other non-hydrogen atoms were refined anisotropically. Use Diamond software to draw crystal structure and bond distance/angle diagram were listed in Table S1-S5.

IR spectra measurements.

IR spectra measurements were performed on the KBr diluted pellets three compounds at room temperature using a Shimadzu model IR-60 spectrometer (Figure. S1).

DSC and dielectric measurement

11.5 mg of polycrystalline sample was measured by Perkin Elmer DSC instrument under nitrogen atmosphere at different temperatures of 250~430 K. The complex permittivity of compound N-Br at different frequencies was measured at 250~430 K and 1.0 V AC voltage on Tonghui TH2828 dielectric meter ε′. And for dielectric studies, the sample pellets were painted silver glue as electrodes.

Powder X-ray Diffraction (PXRD)

The variable temperature PXRD data of compound N-Cl, N-Br and N-I were collected at room temperature using a Rigaku Smartlab X-ray diffractometer with 2θ range of 5-50° in a step size 10° min^{-1}.

Fluorescence measurement

The emission and excitation spectrum of three compounds were measured with the Edinburgh FLS1000 fluorescence and the time-resolved spectrophotometer equipped with a xenon lamp. The photoluminescence quantum efficiency of the compound was characterized by integrating sphere on fluorescence spectrometer. CIE chromaticity coordinates are calculated by CIE software package based on emission spectrum data.

Ferroelastic measurement and spontaneous strain tensor calculation

The evolution of domain structures were observed by using an Olympus BX51TRF polarizing microscope at different temperatures controlled by INSTEC HCC602 cooling / heating device.

Calculation particular matrix is as follows:

$$\varepsilon_{ij}=\begin{bmatrix} \frac{a_{RTP}}{a_{HTP}}\sin\gamma_{RTP}-1 & \frac{1}{2}\left(\frac{a_{RTP}}{a_{HTP}}\cos\gamma_{RTP}\right) & \frac{1}{2}\left(\frac{a_{RTP}\sin\gamma_{RTP}\cos\beta_{HTP}}{a_{HTP}\sin\beta_{HTP}}-\frac{c_{RTP}\sin\alpha_{RTP}\cos\beta_{RTP}}{c_{HTP}\sin\beta_{HTP}}\right) \\ \frac{1}{2}\left(\frac{a_{RTP}}{a_{HTP}}\cos\gamma_{RTP}\right) & \frac{b_{RTP}}{b_{HTP}}-1 & \frac{1}{2}\left(\frac{c_{RTP}\cos\alpha_{RTP}}{c_{HTP}\sin\beta_{HTP}}+\frac{a_{RTP}\cos\beta_{HTP}\cos\gamma_{RTP}}{a_{HTP}\sin\beta_{HTP}}\right) \\ \frac{1}{2}\left(\frac{a_{RTP}\sin\gamma_{RTP}\cos\beta_{HTP}}{a_{HTP}\sin\beta_{HTP}}-\frac{c_{RTP}\sin\alpha_{RTP}\cos\beta_{RTP}}{c_{HTP}\sin\beta_{HTP}}\right) & \frac{1}{2}\left(\frac{c_{RTP}\cos\alpha_{RTP}}{c_{HTP}\sin\beta_{HTP}}+\frac{a_{RTP}\cos\beta_{HTP}\cos\gamma_{RTP}}{a_{HTP}\sin\beta_{HTP}}\right) & \frac{c_{RTP}\sin\alpha_{RTP}\sin\beta_{RTP}}{c_{HTP}\sin\beta_{HTP}}-1 \end{bmatrix}$$

Here, RTP and HTP represent 293 and 413K for compound N-Br, respectively.

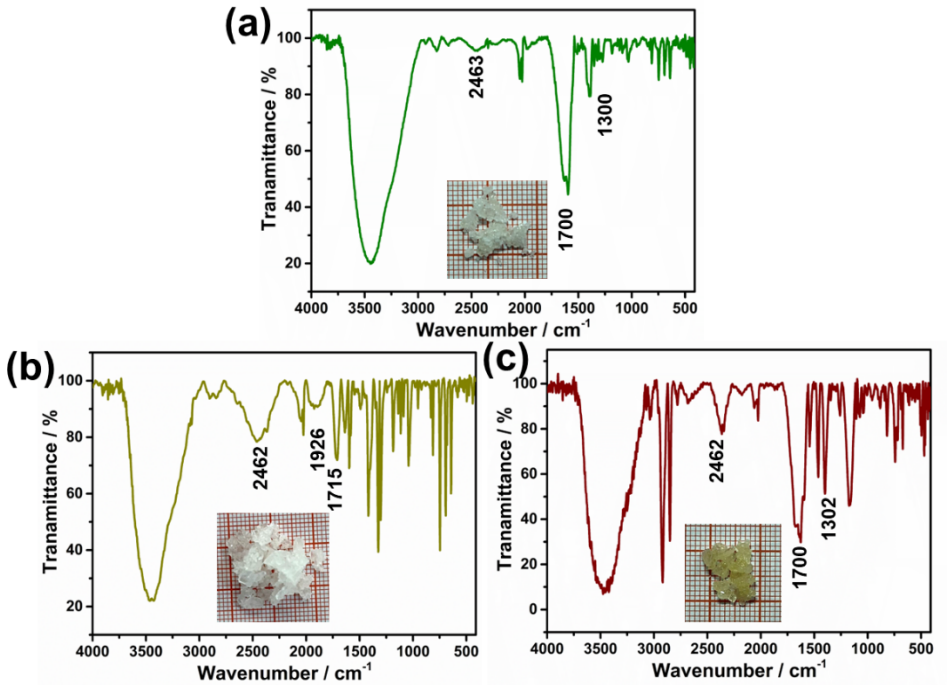

Fig. S1 Infrared spectrums and crystal pictures of N-Cl (a), N-Br (b) and N-I (c). Description: the IR spectrum of three compounds displayed the existence of typical strong stretching vibration peaks (-OH at 3500 cm^{-1}, -COOH at 2463, 1926, 1715 and 1302 cm^{-1}), which could consider as the indirect proof to the nicotinic acid salts crystalline structure we have obtained.

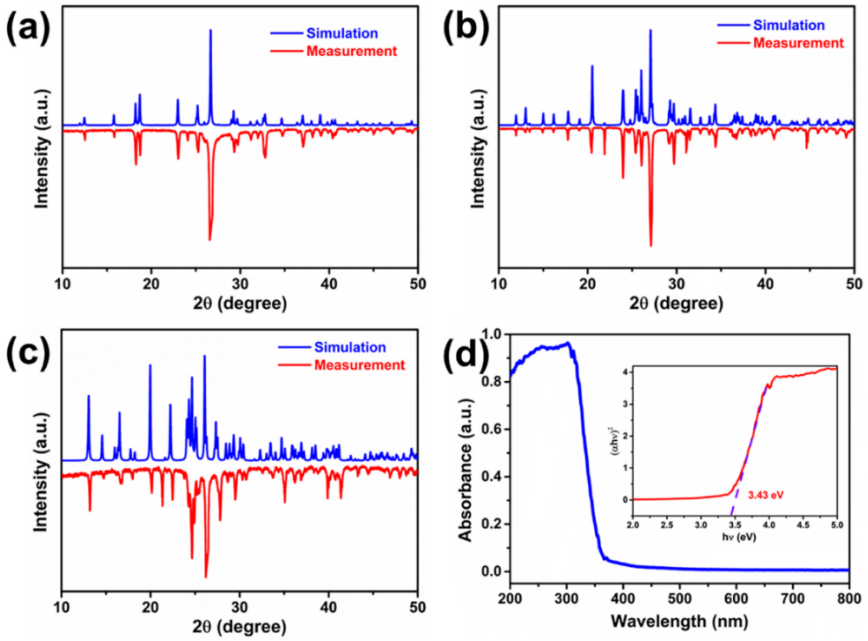

Fig. S2 Experimental PXRD patterns of compound N-Cl (a), N-Br (b) and N-I (c) matching with the simulated ones from crystal structures at room temperature, respectively. UV-vis absorption spectra (d) and the Tauc plot (insert) of compound N-Br at room temperature.

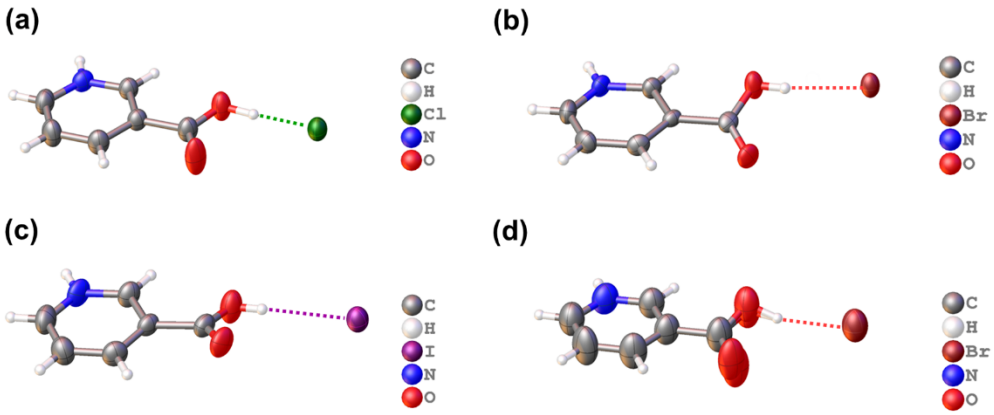

Fig. S3 The non-spherical crystal forms of N-Cl (a), N-Br (b) and N-I (c) at 293 K, respectively, and N-Br (d) at 413 K, showing ADPs of those crystal structures.

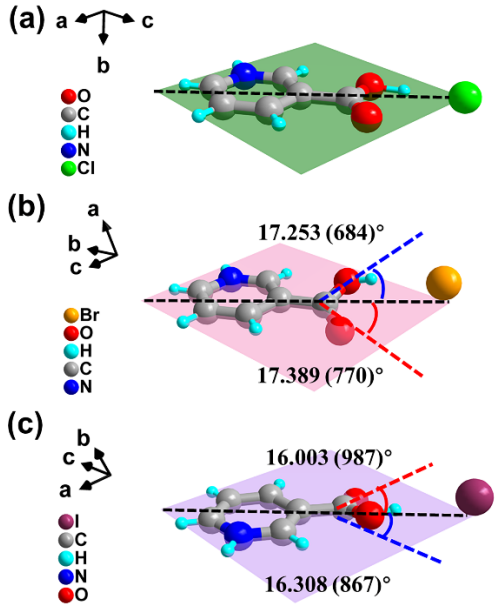

Fig. S4 The asymmetric unit crystal structures of N-Cl (a), N-Br (b) and N-I (c).

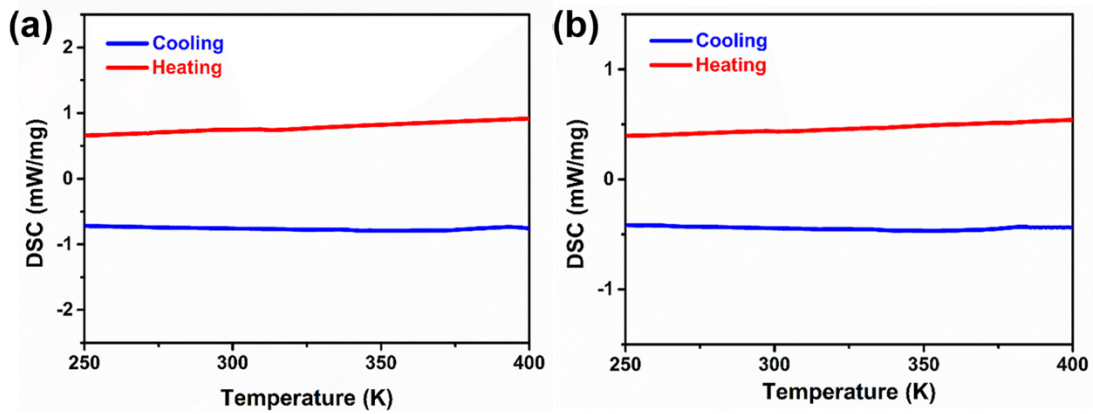

Fig. S5 DSC curves of crystal N-Cl (a) and N-I (b) in the heating-cooling run between 250 K and 400 K.

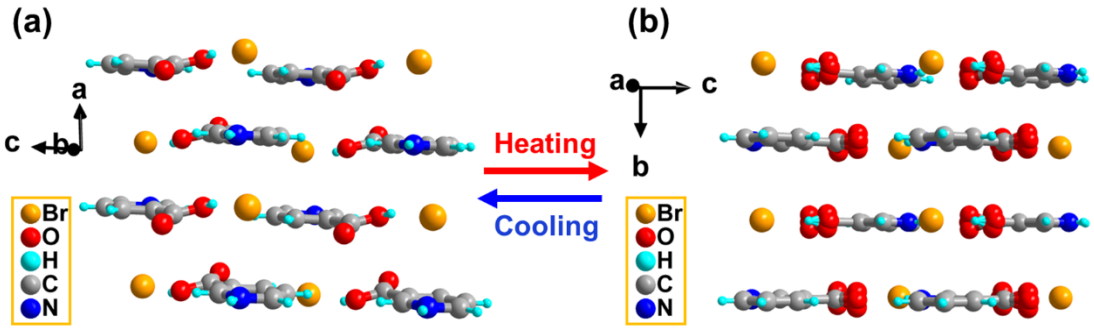

Fig. S6 Packing diagram of N-Br at LTP (a) and HTP (b).

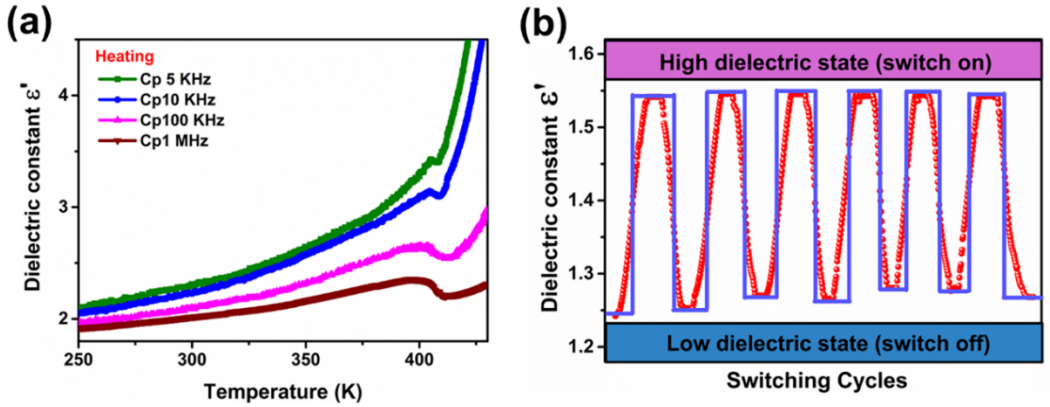

Fig. S7 (a) The real part (ε′) of the dielectric permittivity at various frequencies by different temperatures in the heating mode for the polycrystalline sample N-Br. (b) Thermal bistable dielectric switch periodic measurement after several ON/OFF circles at 1 MHz. For clarity, only the first six switch circles are shown.

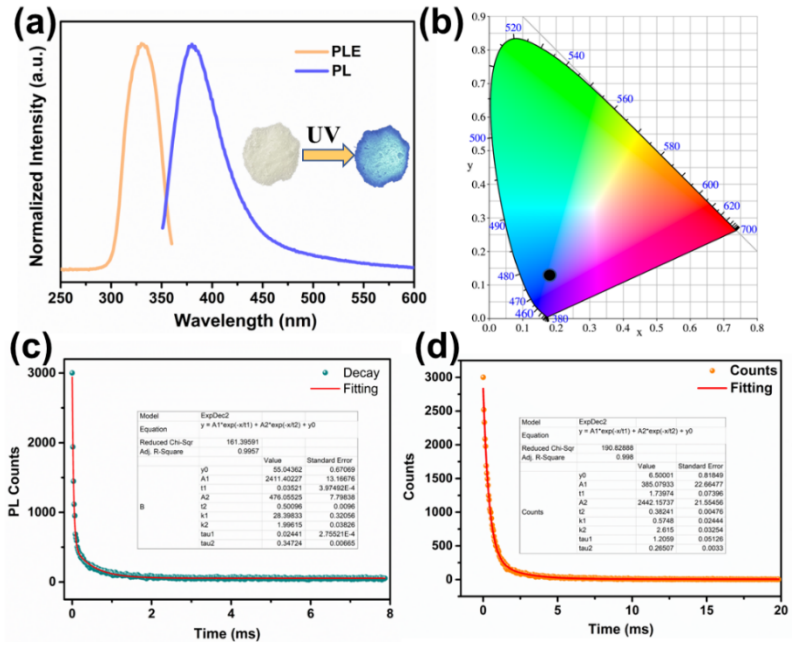

Fig. S8 The luminescence excitation and emission spectra (a) and CIE chromaticity coordinates (b) of compound N-H. The fluorescence lifetime of compound N-Cl (c) and N-Br (d).

Table S1. Crystal data and structure refinements for N-Cl, N-Br, and N-I at different temperatures.

	N-Cl	N-Br		N-I
Temperature	293 K	293 K	413 K	293 K
Empirical formula	$C_6H_6NO_2{\cdot}Cl$	$C_6H_6NO_2{\cdot}Br$	$C_6H_6NO_2{\cdot}Br$	$C_6H_6NO_2{\cdot}I$
Formula weight	159.57	204.02	204.02	251.02
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/m$	$P\bar{1}$	$P2_1/m$	$P\bar{1}$
a/Å	7.1749 (3)	7.0945 (8)	7.4792 (5)	7.4174 (5)
b/Å	6.6728 (3)	7.4389 (6)	6.9912 (7)	7.4195 (7)
c/Å	7.4888 (3)	7.5574 (10)	7.5202 (4)	8.1011 (7)
α/ °	90	79.954 (10)	90	81.904 (7)
β/ °	99.545 (4)	86.332 (10)	100.036 (6)	79.902 (6)
γ/ °	90	68.407 (9)	90	67.021 (7)
V/ Å^3	353.58 (3)	365.15 (7)	387.20 (5)	402.80 (6)
F (000)	164.0	200.0	186.0	236.0
Z	2	2	2	2
Calculated density	1.499 mg m^{-3}	1.856 mg m^{-3}	1.681 mg m^{-3}	2.070 mg m^{-3}
S	1.093	1.074	0.946	1.096
R1 [I>2σ(I)]	0.0288	0.0565	0.0390	0.0358
wR2 [I>2σ(I)]	0.0809	0.1536	0.1075	0.0910

Table S2. Selected bond lengths [Å] and angles [°] for N-Cl at 293 K.

Bond lengths [Å]			
O1—H1	0.98 (4)	C2—C3	1.383 (3)
O1—C6	1.307 (2)	O2—C6	1.195 (2)
N1—H1A	0.87 (3)	C3—H3	0.9300
N1—C1	1.326 (3)	C3—C4	1.383 (3)
N1—C5	1.334 (2)	C4—C5	1.377 (2)

C1—H1B	0.9300	C4—C6	1.495 (2)
C1—C2	1.371 (3)	C5—H5	0.9300
C2—H2	0.9300		
Bond angles [°]			
C6—O1—H1	109 (2)	C4—C3—C2	119.25 (17)
C1—N1—H1A	122.0 (17)	C4—C3—H3	120.4
C1—N1—C5	123.08 (16)	C3—C4—C6	119.74 (16)
C5—N1—H1A	114.9 (17)	C5—C4—C3	119.27 (16)
N1—C1—H1B	120.2	C5—C4—C6	120.99 (17)
N1—C1—C2	119.61 (17)	N1—C5—C4	119.32 (17)
C2—C1—H1B	120.2	N1—C5—H5	120.3
C1—C2—H2	120.3	C4—C5—H5	120.3
C1—C2—C3	119.47 (18)	O1—C6—C4	113.93 (16)
C3—C2—H2	120.3	O2—C6—O1	124.79 (17)
C2—C3—H3	120.4	O2—C6—C4	121.27 (18)
N1—C1—C2—C3	0.000 (1)	C3—C4—C6—O1	180.000 (1)
C1—N1—C5—C4	0.000 (1)	C3—C4—C6—O2	0.000 (1)
C1—C2—C3—C4	0.000 (1)	C5—N1—C1—C2	0.000 (1)
C2—C3—C4—C5	0.000 (1)	C5—C4—C6—O1	0.000 (1)
C2—C3—C4—C6	180.000 (1)	C5—C4—C6—O2	180.000 (1)
C3—C4—C5—N1	0.000 (1)	C6—C4—C5—N1	180.000 (1)

Table S3. Selected bond lengths [Å] and angles [°] for N-Br at 293 K.

Bond lengths [Å]			
O1—H1	0.8200	C2—C3	1.396 (13)
O1—C6	1.325 (10)	O2—C6	1.210 (10)
N1—H1A	0.8600	C3—H3	0.9300
N1—C1	1.338 (12)	C3—C4	1.378 (12)
N1—C5	1.338 (11)	C4—C5	1.369 (12)

C1—H1B	0.9300	C4—C6	1.496 (12)
C1—C2	1.360 (14)	C5—H5	0.9300
C2—H2	0.9300		
Bond angles [°]			
C6—O1—H1	109.5	C4—C3—C2	119.8 (9)
C1—N1—H1A	119.0	C4—C3—H3	120.1
C1—N1—C5	121.9 (8)	C3—C4—C6	120.6 (8)
C5—N1—H1A	119.0	C5—C4—C3	119.0 (8)
N1—C1—H1B	119.8	C5—C4—C6	120.5 (8)
N1—C1—C2	120.4 (9)	N1—C5—C4	120.1 (9)
C2—C1—H1B	119.8	N1—C5—H5	119.9
C1—C2—H2	120.7	C4—C5—H5	119.9
C1—C2—C3	118.7 (9)	O1—C6—C4	113.1 (7)
C3—C2—H2	120.7	O2—C6—O1	124.8 (9)
C2—C3—H3	120.1	O2—C6—C4	122.1 (9)
N1—C1—C2—C3	2.1 (16)	C3—C4—C6—O1	164.0 (9)
C1—N1—C5—C4	1.5 (14)	C3—C4—C6—O2	-16.7 (14)
C1—C2—C3—C4	-1.1 (15)	C5—N1—C1—C2	-2.4 (15)
C2—C3—C4—C5	0.2 (14)	C5—C4—C6—O1	-17.1 (13)
N2—C3—C4—C6	179.2 (9)	C5—C4—C6—O2	162.3 (9)
C3—C4—C5—N1	-0.4 (14)	C6—C4—C5—N1	-179.4 (8)

Table S4. Selected bond lengths [Å] and angles [°] for N-Br at 413 K.

Bond lengths [Å]			
O1—H1	0.930 (3)	O2—C6	1.27 (5)
O1—C6	1.39 (5)	O2A—O2Ai	0.67 (15)
O1A—H1	0.930 (3)	O2A—C6	1.19 (4)
O1A—O1A^{i}	0.65 (10)	C2—H2	0.9300
O1A—C6	1.28 (4)	C2—C3	1.370 (8)

N1—H1A	0.76 (7)	C3—H3	0.9300
N1—C1	1.325 (8)	C3—C4	1.375 (7)
N1—C5	1.316 (7)	C4—C5	1.366 (6)
C1—H1B	0.9300	C4—C6	1.494 (7)
C1—C2	1.365 (8)	C5—H5	0.9300
Bond angles [°]			
C6—O1—H1	97 (6)	C3—C4—C6	120.6 (4)
O1A^{i}—O1A—H1	70 (3)	C5—C4—C3	118.9 (5)
O1A^{i}—O1A—C6	75 (2)	C5—C4—C6	120.5 (5)
C6—O1A—H1	105 (6)	N1—C5—C4	119.8 (5)
C1—N1—H1A	121 (5)	N1—C5—H5	120.1
C5—N1—H1A	116 (5)	C4—C5—H5	120.1
C5—N1—C1	123.1 (5)	O1—C6—C4	111.7 (7)
N1—C1—H1B	120.3	O1A^{i}—C6—C4	115.2 (9)
N1—C1—C2	119.3 (5)	O1A—C6—C4	115.2 (9)
C2—C1—H1B	120.3	O2—C6—O1	131 (3)
O2A^{i}—O2A—C6	74 (3)	O2—C6—O1A^{i}	125 (4)
C1—C2—H2	120.3	O2—C6—C4	117 (3)
C1—C2—C3	119.3 (5)	O2A^{i}—C6—O1A	112 (3)
C3—C2—H2	120.3	O2A—C6—O1A	121 (3)
C2—C3—H3	120.2	O2A^{i}—C6—O2A	33 (7)
C2—C3—C4	119.6 (5)	O2A^{i}—C6—C4	124 (3)
C4—C3—H3	120.2	O2A—C6—C4	124 (3)
O1A^{i}—O1A—C6—O2A	79 (4)	C3—C4—C6—O1A^{i}	164 (2)
O1A^{i}—O1A—C6—O2A^{i}	115 (4)	C3—C4—C6—O1A	−164 (2)
O1A^{i}—O1A—C6—C4	−97.1 (12)	C3—C4—C6—O2	0.000 (15)

N1—C1—C2—C3	0.000 (1)	C3—C4—C6—O2A^{i}	−20 (4)
C1—N1—C5—C4	0.000 (1)	C3—C4—C6—O2A	20 (4)
C1—C2—C3—C4	0.000 (1)	C5—N1—C1—C2	0.000 (1)
O2A^{i}—O2A—C6—O1A^{i}	114 (3)	C5—C4—C6—O1	0.000 (7)
O2A^{i}—O2A—C6—O1A	82 (3)	C5—C4—C6—O1A^{i}	−16 (2)
O2A^{i}—O2A—C6—C4	−101 (2)	C5—C4—C6—O1A	16 (2)
C2—C3—C4—C5	0.000 (1)	C5—C4—C6—O2	180.000 (14)
C2—C3—C4—C6	180.000 (1)	C5—C4—C6—O2A^{i}	160 (4)
C3—C4—C5—N1	0.000 (1)	C5—C4—C6—O2A	−160 (4)
C3—C4—C6—O1	180.000 (7)	C6—C4—C5—N1	180.000 (1)

Symmetry code: (i) *x*, −*y*+3/2, *z*.

Table S5. Selected bond lengths [Å] and angles [°] for N-I at 293 K.

Bond lengths [Å]			
C1—H1	0.9300	C2—C3	1.382 (7)
C1—N1	1.316 (7)	O2—C6	1.205 (5)
C1—C2	1.368 (8)	C3—H3	0.9300
O1—H1A	0.8200	C3—C4	1.383 (7)
O1—C6	1.316 (6)	C4—C5	1.378 (6)
N1—H1B	0.82 (6)	C4—C6	1.497 (6)
N1—C5	1.334 (6)	C5—H5	0.9300
C2—H2	0.9300		
Bond angles [°]			
N1—C1—H1	120.0	C2—C3—C4	119.0 (4)
N1—C1—C2	119.9 (4)	C4—C3—H3	120.5

C2—C1—H1	120.0	C3—C4—C6	120.7 (4)
C6—O1—H1A	109.5	C5—C4—C3	119.4 (4)
C1—N1—H1B	116 (5)	C5—C4—C6	119.9 (4)
C1—N1—C5	123.2 (4)	N1—C5—C4	119.1 (4)
C5—N1—H1B	120 (5)	N1—C5—H5	120.5
C1—C2—H2	120.3	C4—C5—H5	120.5
C1—C2—C3	119.5 (5)	O1—C6—C4	112.5 (4)
C3—C2—H2	120.3	O2—C6—O1	125.6 (4)
C2—C3—H3	120.5	O2—C6—C4	121.9 (4)
C1—N1—C5—C4	−0.8 (8)	C3—C4—C5—N1	0.8 (7)
C1—C2—C3—C4	−0.3 (8)	C3—C4—C6—O1	164.6 (5)
N1—C1—C2—C3	0.3 (9)	C3—C4—C6—O2	−15.1 (7)
C2—C1—N1—C5	0.2 (8)	C5—C4—C6—O1	−17.0 (6)
C2—C3—C4—C5	−0.3 (7)	C5—C4—C6—O2	163.2 (5)
C2—C3—C4—C6	178.0 (5)	C6—C4—C5—N1	−177.5 (4)