Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

A high-temperature multiaxial precision time-delayed dielectric switch crystal triggered by linear/propeller/ball three forms motion

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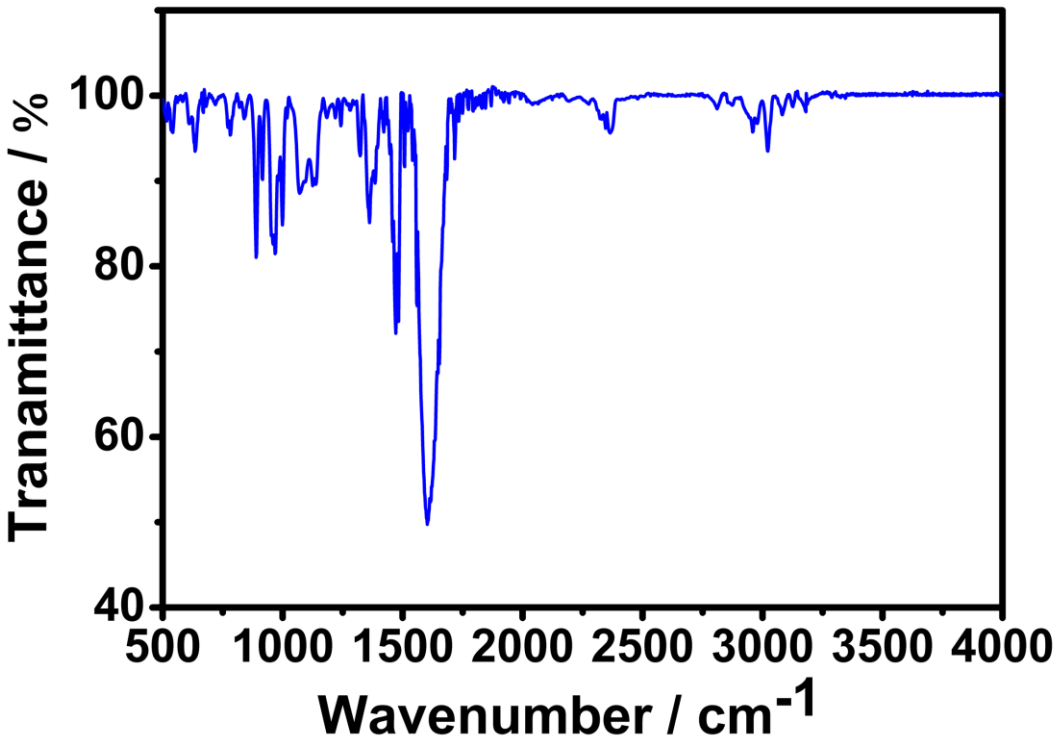

Fig. S1. Infrared spectrum of $(TMAA)_3$-Bi_2Cl_9 in KBr pellets was recorded on a Shimadzu model IR-60 spectrometer at room temperature.

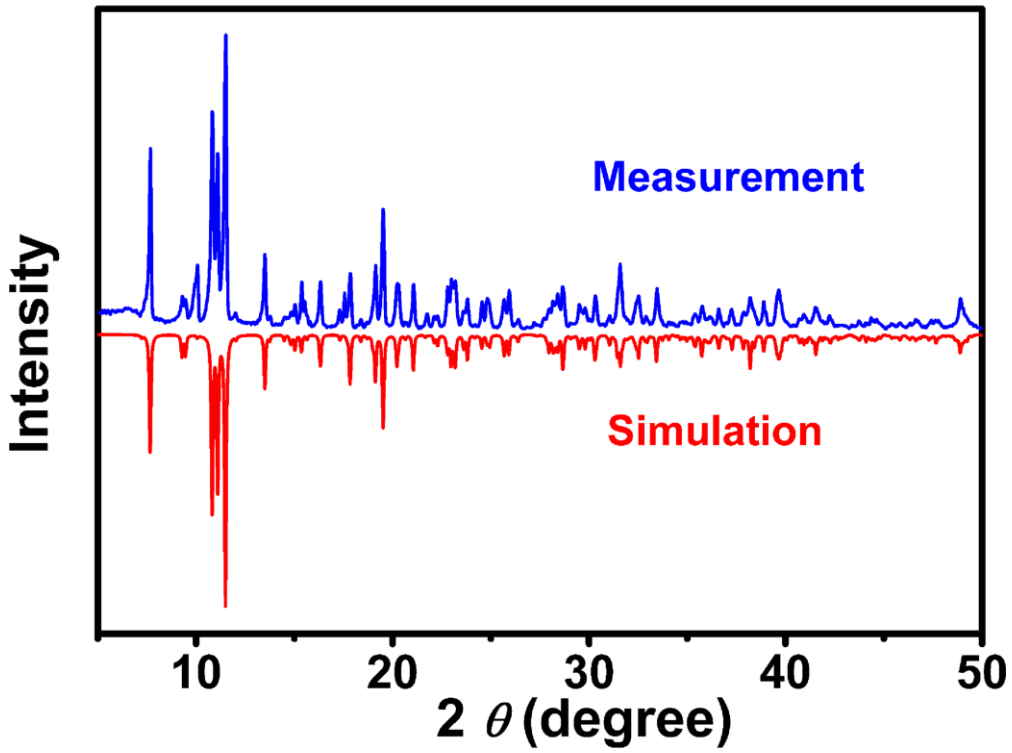

Fig. S2. Powder X-ray diffraction patterns (PXRD) of $(TMAA)_3$-Bi_2Cl_9 at room temperature.

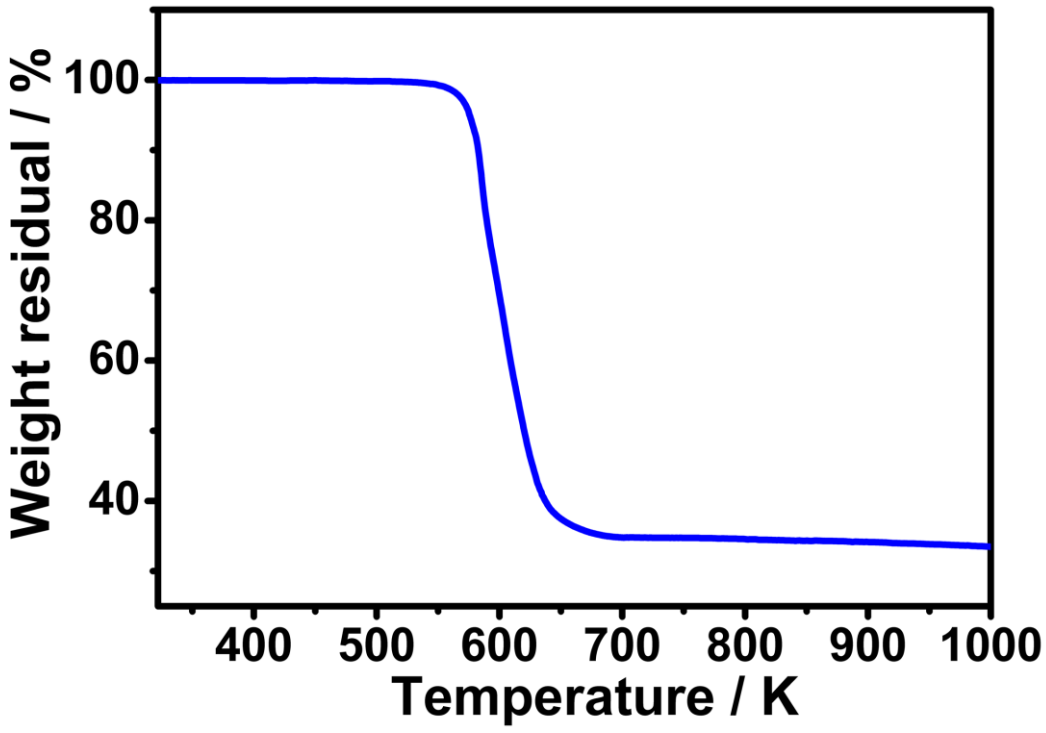

Fig. S3. TGA curves for $(TMAA)_3$-Bi_2Cl_9.

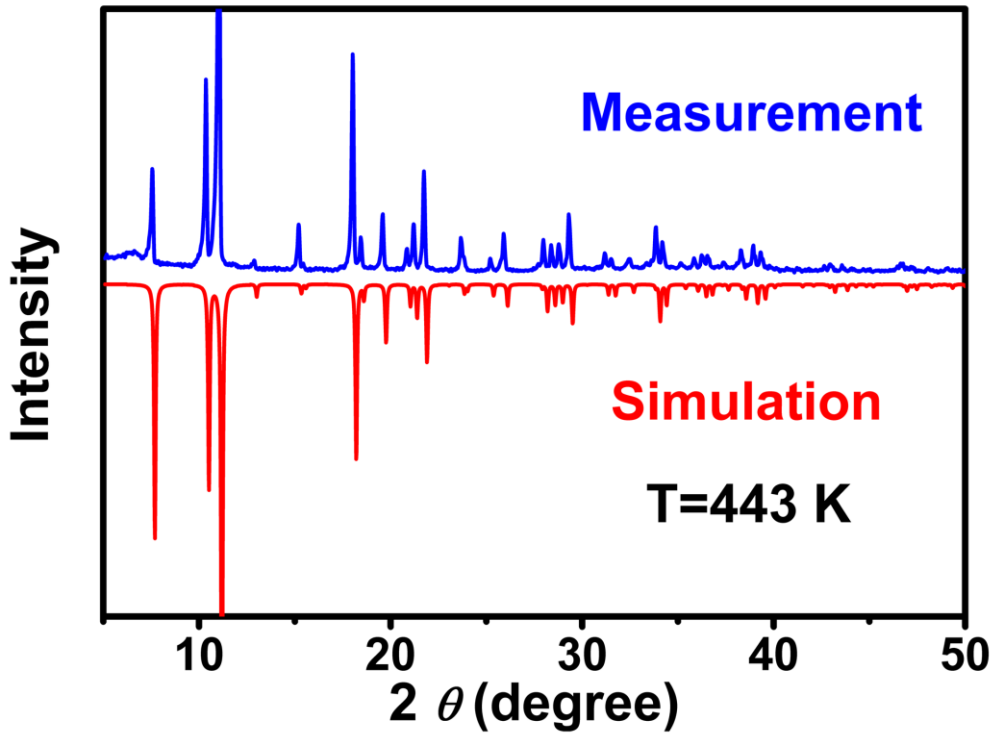

Fig. S4 Experimental variable-temperature PXRD patterns measured at 443 K of $(TMAA)_3$-Bi_2Cl_9 match well with the simulated ones.

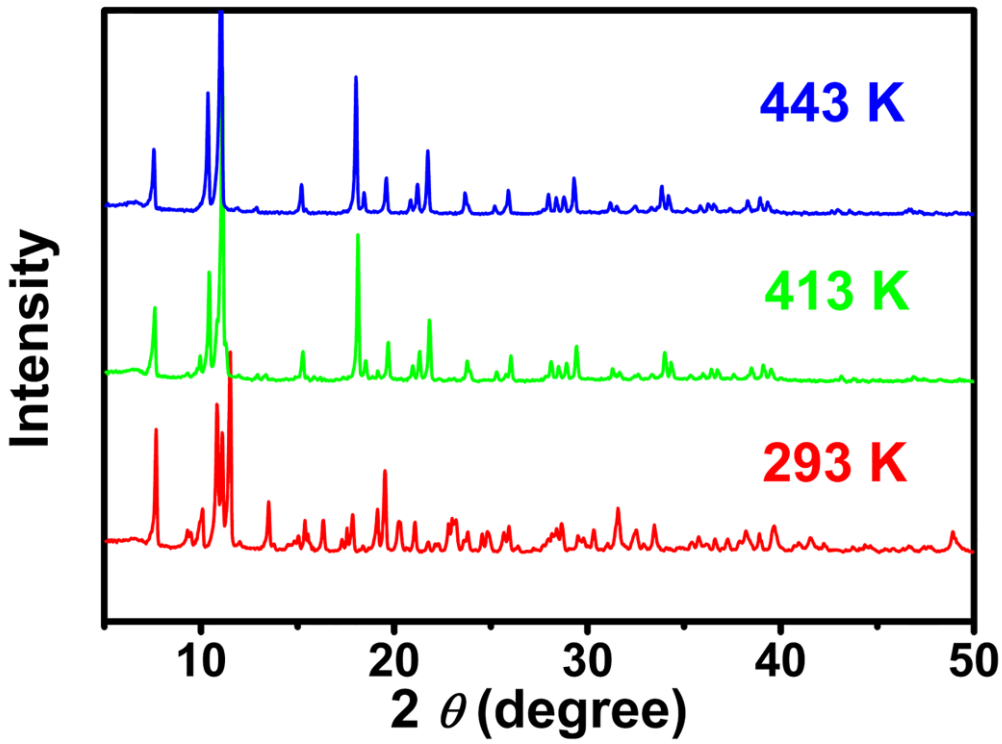

Fig. S5 Variable-temperature PXRD patterns of $(TMAA)_3$-Bi_2Cl_9.

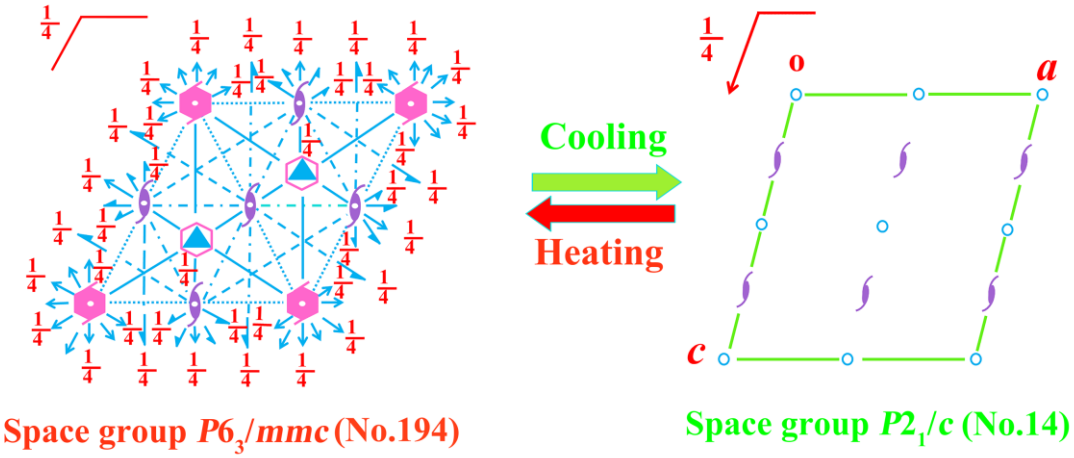

Fig. S6 The symmetry breaking of $(TMAA)_3$-Bi_2Cl_9 from HTP to RTP.

Table S1 The crystallographic data and structure refinements of $[TMAA]_3[Bi_2Cl_9]$ at 293 K and 443 K

Temperature	RTP (293K)	HTP (443K)
Empirical formula	$[TMAA]_3[Bi_2Cl_9]$	$[C_{15}N_3][Bi_2Cl_9]$
Formula weight	1037.56	945.3
Crystal system	Monoclinic	Hexagonal
Space group	$P2_1/c$	$P6_3/mmc$
a / Å	12.1075(6)	9.7795(9)
b / Å	15.9308(7)	9.7795(9)
c / Å	20.0007(14)	23.197(5)
α /°	90.00	90.00
β /°	107.869(5)	90.00
γ /°	90.00	120.00

V / Å^3	3671.7(4)	1921.3(5)
Z	4	2
F (000)	1960	916.0
Reflns measured	19012	7909
Independent reflns	6195	692
Reflns used	12082	809
GOF	1.129	1.026
$R_1[I > 2\sigma(I)]$	0.0443	0.1328
wR_2 $[I > 2\sigma(I)]$	0.1339	0.3818

Table S2 Bond lengths [Å] for $[TMAA]_3[Bi_2Cl_9]$ at 293 K and 443 K

293 K		443 K	
N1—C2	1.482 (3)	N1—C2^{i}	1.3002 (16)
N1—C3	1.432 (11)	N1—C2	1.3002 (16)
N1—C1	1.444 (11)	N1—C1^{i}	1.500 (2)
N1—C4	1.506 (8)	N1—C1^{ii}	1.500 (2)
C1—H1A	0.9600	N1—C1	1.500 (2)
C1—H1B	0.9600	C1—C2^{i}	1.985 (2)
C1—H1C	0.9600	C1—C2	1.985 (2)
C2—H2A	0.9600	C2—C3	1.300 (2)
C2—H2B	0.9600	C2—C1^{i}	1.985 (2)
C2—H2C	0.9600	C2—C1^{ii}	1.985 (2)
C3—H3A	0.9600	C4—C3	1.300 (3)
C3—H3B	0.9600	N2—C6^{iii}	1.4000 (13)
C3—H3C	0.9600	N2—C6	1.4000 (13)
C4—C5	1.498 (4)	N2—C5^{iv}	1.500 (3)
C4—H4A	0.9700	N2—C5^{iii}	1.500 (3)
C4—H4B	0.9700	N2—C5^{v}	1.500 (3)
C5—C6	1.328 (14)	N2—C5^{vi}	1.500 (3)
C5—H5	0.9300	N2—C5	1.500 (3)
C6—H6A	0.9300	N2—C5^{vii}	1.500 (3)
C6—H6B	0.9300	C5—C5^{iv}	1.268 (10)
N2—C7	1.484 (4)	C5—C5^{vii}	1.720 (6)

N2—C9	1.402 (8)	C6—C7	1.300 (2)
N2—C8	1.423 (11)	C7—C8	1.300 (3)
N2—C10	1.496 (9)	Bi1—Cl2^{viii}	2.50 (3)
C7—H7A	0.9600	Bi1—Cl2^{ix}	2.50 (3)
C7—H7B	0.9600	Bi1—Cl2	2.50 (3)
C7—H7C	0.9600	Bi1—Cl1^{ix}	2.806 (4)
C8—H8A	0.9600	Bi1—Cl1	2.806 (4)
C8—H8B	0.9600	Bi1—Cl1^{x}	2.806 (4)
C8—H8C	0.9600	Cl1—Bi1^{x}	2.806 (4)
C9—H9A	0.9600		
C9—H9B	0.9600		
C9—H9C	0.9600		
C10—C11	1.508 (4)		
C10—H10A	0.9700		
C10—H10B	0.9700		
C11—C12	1.374 (4)		
C11—H11	0.9300		
C12—H12A	0.9300		
C12—H12B	0.9300		
N3—C13	1.468 (6)		
N3—C16	1.472 (7)		
N3—C15	1.482 (8)		
N3—C14	1.503 (5)		
C13—H13A	0.9600		
C13—H13B	0.9600		
C13—H13C	0.9600		
C14—H14A	0.9600		
C14—H14B	0.9600		
C14—H14C	0.9600		
C15—H15A	0.9600		
C15—H15B	0.9600		
C15—H15C	0.9600		
C16—C17	1.578 (10)		
C16—H16A	0.9700		
C16—H16B	0.9700		
C17—C18	1.246 (12)		
C17—H17	0.9300		
C18—H18A	0.9300		
C18—H18B	0.9300		
Bi1—Cl8	2.5647 (15)		
Bi1—Cl6	2.5675 (15)		
Bi1—Cl7	2.5761 (14)		
Bi1—Cl4	2.8747 (13)		
Bi1—Cl9	2.8947 (15)		

Bi1—Cl5	2.9108 (13)
Bi2—Cl3	2.5594 (15)
Bi2—Cl2	2.5684 (17)
Bi2—Cl1	2.5771 (15)
Bi2—Cl5	2.8936 (15)
Bi2—Cl9	2.9002 (13)
Bi2—Cl4	2.9268 (13)

Table S3 Bond angles [°] for $[TMAA]_3[Bi_2Cl_9]$ at 293 and 443 K

293 K		443 K	
C2—N1—C3	102.5 (6)	$C2^{i}$—N1—C2	180.0
C2—N1—C1	116.4 (6)	$C2^{i}$—N1—$C1^{i}$	90.0
C3—N1—C1	110.0 (7)	C2—N1—$C1^{i}$	90.0
C2—N1—C4	117.4 (5)	$C2^{i}$—N1—$C1^{ii}$	90.000 (1)
C3—N1—C4	89.3 (4)	C2—N1—$C1^{ii}$	90.000 (1)
C1—N1—C4	116.1 (7)	$C1^{i}$—N1—$C1^{ii}$	120.000 (1)
N1—C1—H1A	109.5	$C2^{i}$—N1—C1	90.0
N1—C1—H1B	109.5	C2—N1—C1	90.000 (1)
H1A—C1—H1B	109.5	$C1^{i}$—N1—C1	120.0
N1—C1—H1C	109.5	$C1^{ii}$—N1—C1	120.0
H1A—C1—H1C	109.5	N1—C1—$C2^{i}$	40.91 (5)
H1B—C1—H1C	109.5	N1—C1—C2	40.91 (5)
N1—C2—H2A	109.5	$C2^{i}$—C1—C2	81.83 (11)
N1—C2—H2B	109.5	C3—C2—N1	180.0
H2A—C2—H2B	109.5	C3—C2—$C1^{i}$	130.91 (5)
N1—C2—H2C	109.5	N1—C2—$C1^{i}$	49.09 (5)
H2A—C2—H2C	109.5	C3—C2—$C1^{ii}$	130.91 (5)
H2B—C2—H2C	109.5	N1—C2—$C1^{ii}$	49.09 (5)
N1—C3—H3A	109.5	$C1^{i}$—C2—$C1^{ii}$	81.76 (8)
N1—C3—H3B	109.5	C3—C2—C1	130.91 (5)
H3A—C3—H3B	109.5	N1—C2—C1	49.09 (5)
N1—C3—H3C	109.5	$C1^{i}$—C2—C1	81.76 (8)
H3A—C3—H3C	109.5	$C1^{ii}$—C2—C1	81.76 (8)
H3B—C3—H3C	109.5	C4—C3—C2	180.0
C5—C4—N1	95.5 (5)	$C6^{iii}$—N2—C6	180.0
C5—C4—H4A	112.6	$C6^{iii}$—N2—$C5^{iv}$	90.000 (2)
N1—C4—H4A	112.7	C6—N2—$C5^{iv}$	90.000 (2)
C5—C4—H4B	112.7	$C6^{iii}$—N2—$C5^{iii}$	90.000 (2)
N1—C4—H4B	112.7	C6—N2—$C5^{iii}$	90.000 (2)
H4A—C4—H4B	110.1	$C5^{iv}$—N2—$C5^{iii}$	70.0 (4)
C6—C5—C4	108.0 (9)	$C6^{iii}$—N2—$C5^{v}$	90.0

C6—C5—H5	126.0	C6—N2—C5^{v}	90.0
C4—C5—H5	126.0	C5^{iv}—N2—C5^{v}	120.000 (3)
C5—C6—H6A	120.0	C5^{iii}—N2—C5^{v}	50.0 (4)
C5—C6—H6B	120.0	C6^{iii}—N2—C5^{vi}	90.000 (2)
H6A—C6—H6B	120.0	C6—N2—C5^{vi}	90.000 (2)
C7—N2—C9	122.9 (6)	C5^{iv}—N2—C5^{vi}	170.0 (4)
C7—N2—C8	113.7 (7)	C5^{iii}—N2—C5^{vi}	120.000 (1)
C9—N2—C8	118.4 (7)	C5^{v}—N2—C5^{vi}	70.0 (4)
C7—N2—C10	95.7 (5)	C6^{iii}—N2—C5	90.000 (1)
C9—N2—C10	98.1 (5)	C6—N2—C5	90.000 (1)
C8—N2—C10	98.8 (7)	C5^{iv}—N2—C5	50.0 (4)
N2—C7—H7A	109.5	C5^{iii}—N2—C5	120.000 (1)
N2—C7—H7B	109.5	C5^{v}—N2—C5	170.0 (4)
H7A—C7—H7B	109.5	C5^{vi}—N2—C5	120.000 (2)
N2—C7—H7C	109.5	C6^{iii}—N2—C5^{vii}	90.000 (1)
H7A—C7—H7C	109.5	C6—N2—C5^{vii}	90.000 (1)
H7B—C7—H7C	109.5	C5^{iv}—N2—C5^{vii}	120.0
N2—C8—H8A	109.5	C5^{iii}—N2—C5^{vii}	170.0 (4)
N2—C8—H8B	109.5	C5^{v}—N2—C5^{vii}	120.000 (1)
H8A—C8—H8B	109.5	C5^{vi}—N2—C5^{vii}	50.0 (4)
N2—C8—H8C	109.5	C5—N2—C5^{vii}	70.0 (4)
H12A—C12—H12B	120.0	C5^{iv}—C5—N2	64.99 (18)
C13—N3—C16	104.7 (5)	C5^{iv}—C5—C5^{vii}	120.0
C13—N3—C15	110.6 (5)	N2—C5—C5^{vii}	55.01 (18)
C16—N3—C15	110.4 (5)	C7—C6—N2	180.0
C13—N3—C14	110.9 (4)	C6—C7—C8	180.000 (1)
C16—N3—C14	110.7 (4)	Cl2^{viii}—Bi1—Cl2^{ix}	94.7 (7)
C15—N3—C14	109.4 (5)	Cl2^{viii}—Bi1—Cl2	94.7 (7)
N3—C13—H13A	109.5	Cl2^{ix}—Bi1—Cl2	94.7 (7)
N3—C13—H13B	109.5	Cl2^{viii}—Bi1—Cl1^{ix}	92.7 (4)
H13A—C13—H13B	109.5	Cl2^{ix}—Bi1—Cl1^{ix}	169.0 (5)
N3—C13—H13C	109.5	Cl2—Bi1—Cl1^{ix}	92.7 (4)
H13A—C13—H13C	109.5	Cl2^{viii}—Bi1—Cl1	92.7 (4)
H13B—C13—H13C	109.5	Cl2^{ix}—Bi1—Cl1	92.7 (4)
N3—C14—H14A	109.5	Cl2—Bi1—Cl1	169.0 (5)
N3—C14—H14B	109.5	Cl1^{ix}—Bi1—Cl1	78.83 (14)
H14A—C14—H14B	109.5	Cl2^{viii}—Bi1—Cl1^{x}	169.0 (5)
N3—C14—H14C	109.5	Cl2^{ix}—Bi1—Cl1^{x}	92.7 (4)
H14A—C14—H14C	109.5	Cl2—Bi1—Cl1^{x}	92.7 (4)
H14B—C14—H14C	109.5	Cl1^{ix}—Bi1—Cl1^{x}	78.83 (14)
N3—C15—H15A	109.5	Cl1—Bi1—Cl1^{x}	78.83 (14)
N3—C15—H15B	109.5	Bi1^{x}—Cl1—Bi1	85.70 (18)
H15A—C15—H15B	109.5	C2—N1—C1—C2^{i}	180.0
N3—C15—H15C	109.5	C1^{i}—N1—C1—C2^{i}	−90.0

H15A—C15—H15C	109.5	C1^{ii}—N1—C1—C2^{i}	90.0
H15B—C15—H15C	109.5	C2^{i}—N1—C1—C2	180.0
N3—C16—C17	109.6 (6)	C1^{i}—N1—C1—C2	90.0
N3—C16—H16A	109.7	C1^{ii}—N1—C1—C2	−90.0
C17—C16—H16A	109.7	C2^{i}—N1—C2—C3	0(49)
N3—C16—H16B	109.7	C1^{i}—N1—C2—C3	−120 (65)
C17—C16—H16B	109.7	C1^{ii}—N1—C2—C3	120 (40)
H16A—C16—H16B	108.2	C1—N1—C2—C3	0(40)
C18—C17—C16	122.0 (8)	C2^{i}—N1—C2—C1^{i}	59 (44)
C18—C17—H17	119.0	C1^{ii}—N1—C2—C1^{i}	−120.0
C16—C17—H17	119.0	C1—N1—C2—C1^{i}	120.0
C17—C18—H18A	120.0	C2^{i}—N1—C2—C1^{ii}	179 (44)
C17—C18—H18B	120.0	C1^{i}—N1—C2—C1^{ii}	120.0
H18A—C18—H18B	120.0	C1—N1—C2—C1^{ii}	−120.0
Cl8—Bi1—Cl6	93.62 (6)	C2^{i}—N1—C2—C1	−61 (55)
Cl8—Bi1—Cl7	93.49 (5)	C1^{i}—N1—C2—C1	−120.0
Cl6—Bi1—Cl7	93.89 (5)	C1^{ii}—N1—C2—C1	120.0
Cl8—Bi1—Cl4	93.80 (4)	N1—C1—C2—C3	180.0
Cl6—Bi1—Cl4	91.41 (5)	C2^{i}—C1—C2—C3	180.0
Cl7—Bi1—Cl4	170.70 (4)	C2^{i}—C1—C2—N1	0.0
Cl8—Bi1—Cl9	172.35 (4)	N1—C1—C2—C1^{i}	−41.40 (3)
Cl6—Bi1—Cl9	92.45 (5)	C2^{i}—C1—C2—C1^{i}	−41.40 (3)
Cl7—Bi1—Cl9	90.74 (5)	N1—C1—C2—C1^{ii}	41.40 (3)
Cl4—Bi1—Cl9	81.39 (4)	C2^{i}—C1—C2—C1^{ii}	41.40 (3)
Cl8—Bi1—Cl5	93.92 (5)	N1—C2—C3—C4	0(51)
Cl6—Bi1—Cl5	169.80 (5)	C1^{i}—C2—C3—C4	0(47)
Cl7—Bi1—Cl5	92.48 (4)	C1^{ii}—C2—C3—C4	0(61)
Cl4—Bi1—Cl5	81.25 (4)	C1—C2—C3—C4	0(57)
Cl9—Bi1—Cl5	79.51 (4)	C6^{iii}—N2—C5—C5^{iv}	90.0
H8A—C8—H8C	109.5	C6—N2—C5—C5^{iv}	−90.0
H8B—C8—H8C	109.5	C5^{iii}—N2—C5—C5^{iv}	0.0
N2—C9—H9A	109.5	C5^{v}—N2—C5—C5^{iv}	0.0
N2—C9—H9B	109.5	C5^{vi}—N2—C5—C5^{iv}	180.0
H9A—C9—H9B	109.5	C5^{vii}—N2—C5—C5^{iv}	180.0
N2—C9—H9C	109.5	C6^{iii}—N2—C5—C5^{vii}	−90.0
H9A—C9—H9C	109.5	C6—N2—C5—C5^{vii}	90.0
H9B—C9—H9C	109.5	C5^{iv}—N2—C5—C5^{vii}	180.0
N2—C10—C11	103.0 (4)	C5^{iii}—N2—C5—C5^{vii}	180.0
N2—C10—H10A	111.2	C5^{v}—N2—C5—C5^{vii}	180.0
C11—C10—H10A	111.2	C5^{vi}—N2—C5—C5^{vii}	0.0
N2—C10—H10B	111.2	C6^{iii}—N2—C6—C7	0(40)
C11—C10—H10B	111.2	C5^{iv}—N2—C6—C7	−178 (56)
H10A—C10—H10B	109.1	C5^{iii}—N2—C6—C7	112 (44)
C12—C11—C10	147.6 (6)	C5^{v}—N2—C6—C7	62 (44)

C12—C11—H11	106.2	C5^{vi}—N2—C6—C7	−8(44)
C10—C11—H11	106.2	C5—N2—C6—C7	−128 (56)
C11—C12—H12A	120.0	C5^{vii}—N2—C6—C7	−58 (56)
C11—C12—H12B	120.0	N2—C6—C7—C8	0(49)
Cl3—Bi2—Cl2	94.16 (6)	Cl2^{viii}—Bi1—Cl1—Bi1^{x}	132.6 (3)
Cl3—Bi2—Cl1	92.78 (5)	Cl2^{ix}—Bi1—Cl1—Bi1^{x}	−132.6 (3)
Cl2—Bi2—Cl1	95.25 (6)	Cl2—Bi1—Cl1—Bi1^{x}	0.000 (7)
Cl3—Bi2—Cl5	91.23 (5)	Cl1^{ix}—Bi1—Cl1—Bi1^{x}	40.33 (5)
Cl2—Bi2—Cl5	169.01 (4)	Cl1^{x}—Bi1—Cl1—Bi1^{x}	−40.33 (5)
Cl1—Bi2—Cl5	94.05 (5)		
Cl3—Bi2—Cl9	93.22 (4)		
Cl2—Bi2—Cl9	90.42 (5)		
Cl1—Bi2—Cl9	171.43 (5)		
Cl5—Bi2—Cl9	79.71 (4)		
Cl3—Bi2—Cl4	170.44 (5)		
Cl2—Bi2—Cl4	93.02 (5)		
Cl1—Bi2—Cl4	92.84 (5)		
Cl5—Bi2—Cl4	80.67 (4)		
Cl9—Bi2—Cl4	80.42 (4)		
Bi1—Cl4—Bi2	83.48 (4)		
Bi2—Cl5—Bi1	83.43 (4)		
Bi1—Cl9—Bi2	83.60 (4)		
C2—N1—C4—C5	50.1 (8)		
C3—N1—C4—C5	153.9 (5)		
C1—N1—C4—C5	−94.1 (8)		
N1—C4—C5—C6	−162.6 (9)		
C7—N2—C10—C11	−155.6 (5)		
C9—N2—C10—C11	−31.1 (6)		
C8—N2—C10—C11	89.4 (6)		
N2—C10—C11—C12	102.3 (10)		
C13—N3—C16—C17	−50.4 (7)		
C15—N3—C16—C17	68.7 (8)		
C14—N3—C16—C17	−169.9 (6)		
N3—C16—C17—C18	125.0 (9)		
Cl8—Bi1—Cl4—Bi2	133.65 (4)		
Cl6—Bi1—Cl4—Bi2	−132.62 (5)		
Cl7—Bi1—Cl4—Bi2	−7.8 (3)		
Cl9—Bi1—Cl4—Bi2	−40.36 (4)		
Cl5—Bi1—Cl4—Bi2	40.26 (4)		
Cl3—Bi2—Cl4—Bi1	−8.3 (3)		
Cl2—Bi2—Cl4—Bi1	130.32 (5)		
Cl1—Bi2—Cl4—Bi1	−134.27 (5)		
Cl5—Bi2—Cl4—Bi1	−40.63 (4)		
Cl9—Bi2—Cl4—Bi1	40.40 (4)		

Cl3—Bi2—Cl5—Bi1	−134.88 (4)
Cl2—Bi2—Cl5—Bi1	−15.5 (3)
Cl1—Bi2—Cl5—Bi1	132.25 (5)
Cl9—Bi2—Cl5—Bi1	−41.83 (4)
Cl4—Bi2—Cl5—Bi1	40.03 (4)
Cl8—Bi1—Cl5—Bi2	−134.07 (4)
Cl6—Bi1—Cl5—Bi2	3.6 (3)
Cl7—Bi1—Cl5—Bi2	132.26 (5)
Cl4—Bi1—Cl5—Bi2	−40.83 (4)
Cl9—Bi1—Cl5—Bi2	41.96 (4)
Cl8—Bi1—Cl9—Bi2	−10.6 (4)
Cl6—Bi1—Cl9—Bi2	131.86 (4)
Cl7—Bi1—Cl9—Bi2	−134.22 (4)
Cl4—Bi1—Cl9—Bi2	40.80 (4)
Cl5—Bi1—Cl9—Bi2	−41.83 (4)
Cl3—Bi2—Cl9—Bi1	132.77 (5)
Cl2—Bi2—Cl9—Bi1	−133.04 (5)
Cl1—Bi2—Cl9—Bi1	−1.5 (3)
Cl5—Bi2—Cl9—Bi1	42.10 (4)
Cl4—Bi2—Cl9—Bi1	−40.05 (4)

Symmetry codes: (i) −x+y, −x+1, −z+1/2; (ii) −y+1, x−y+1, z; (iii) −x+y+1, −x+2, −z+1/2; (iv) −x+y+1, y, z; (v) x, x−y+1, −z+1/2; (vi) −y+2, x−y+1, z; (vii) −y+2, −x+2, −z+1/2; (viii) −x+y+1, −x+1, z; (ix) −y+1, x−y, z; (x) −x+y+1, −x+1, −z+1/2.