Structural Diversity and Giant Birefringence in Cyanates BaCNOX (X = Cl, Br, I, and CNO) Containing Linear π-Conjugated Units: A Combined Experimental and Theoretical Study

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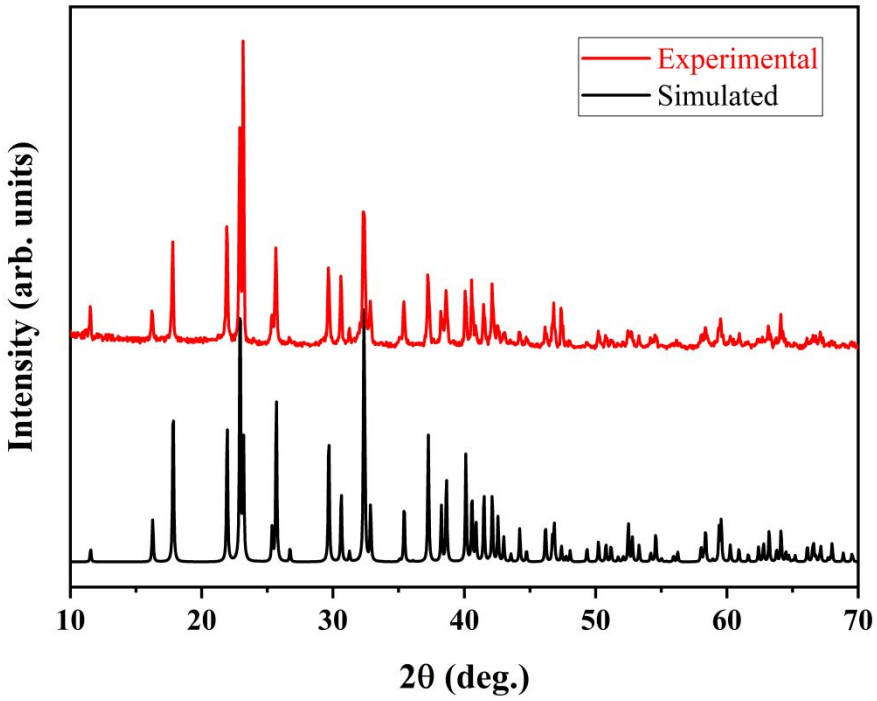

Figure S1. Powder X-ray diffraction patterns of BaCNOCl.

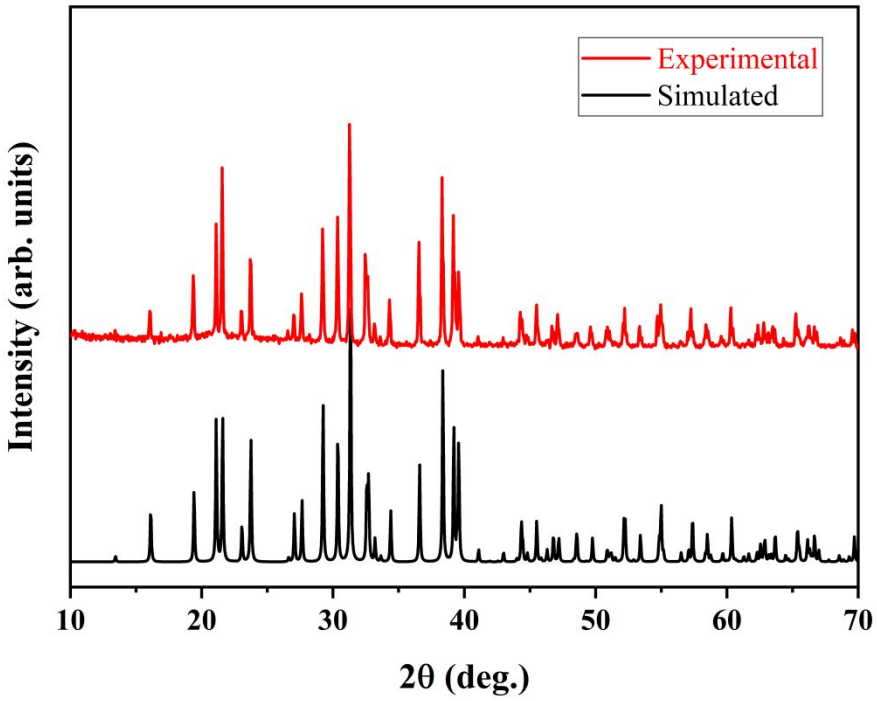

Figure S2. Powder X-ray diffraction patterns of BaCNOBr.

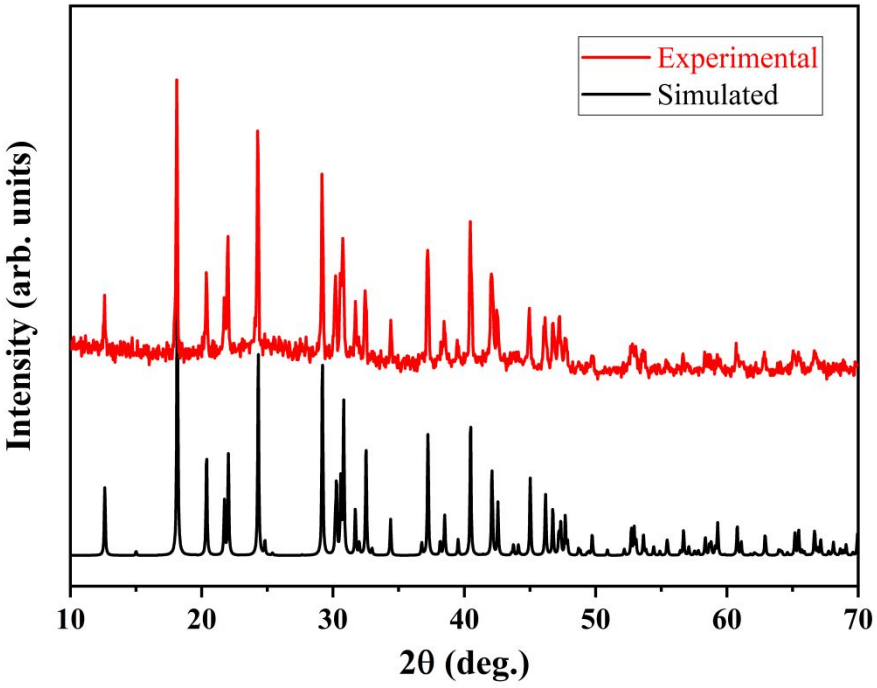

Figure S3. Powder X-ray diffraction patterns of $Ba(CNO)_2$.

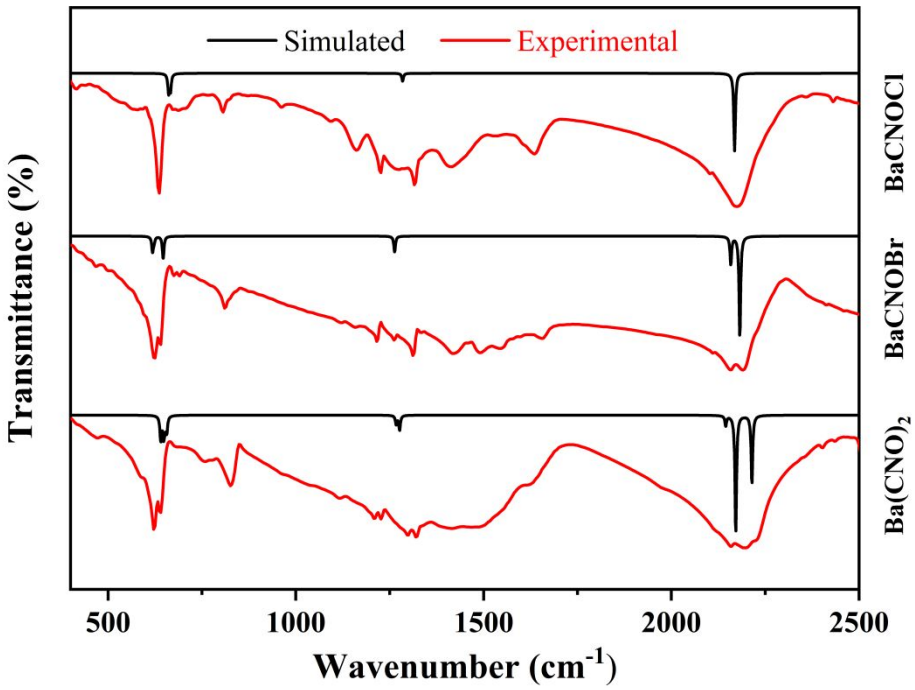

Figure S4. The infrared spectra of BaCNOX (X = Cl, Br, CNO).

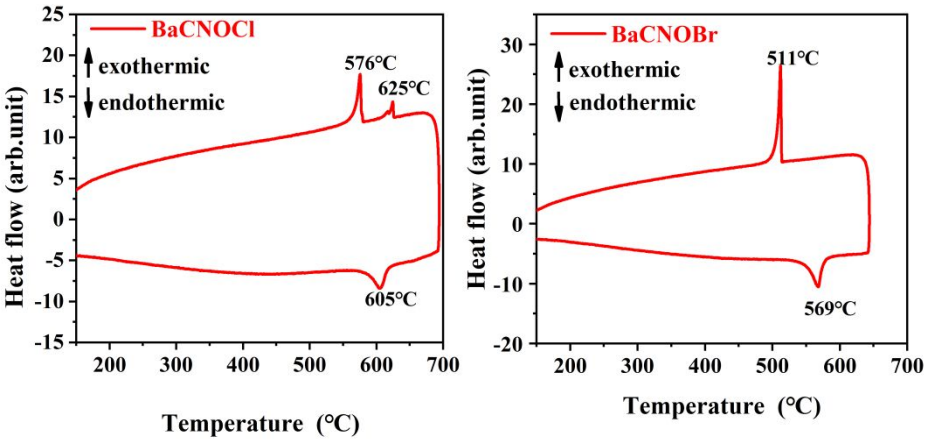

Figure S5. DSC curves for BaCNOCl and BaCNOBr.

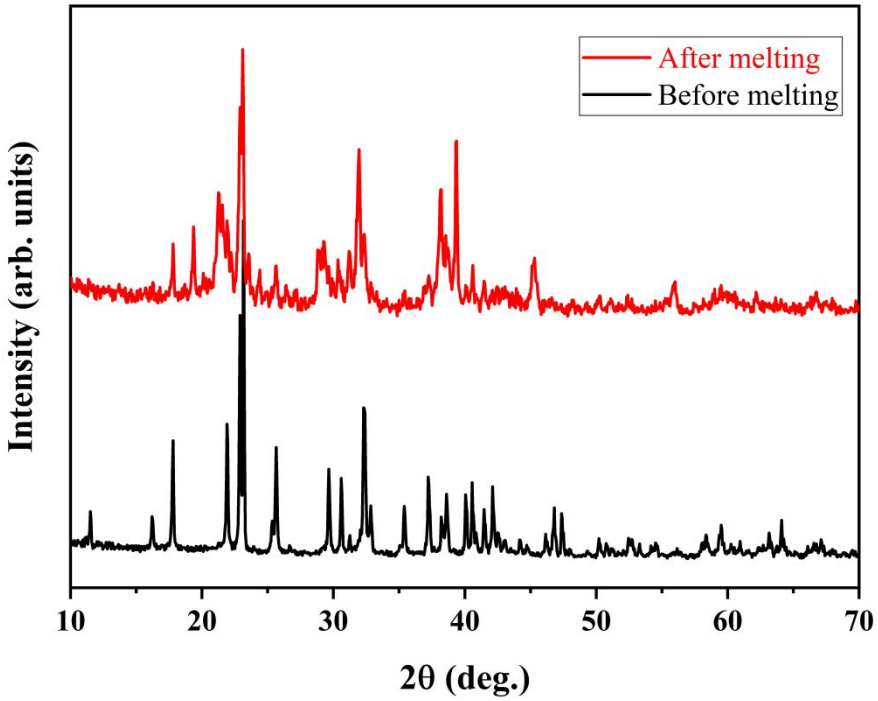

Figure S6. Powder X-ray diffraction patterns of BaCNOCl before and after melting.

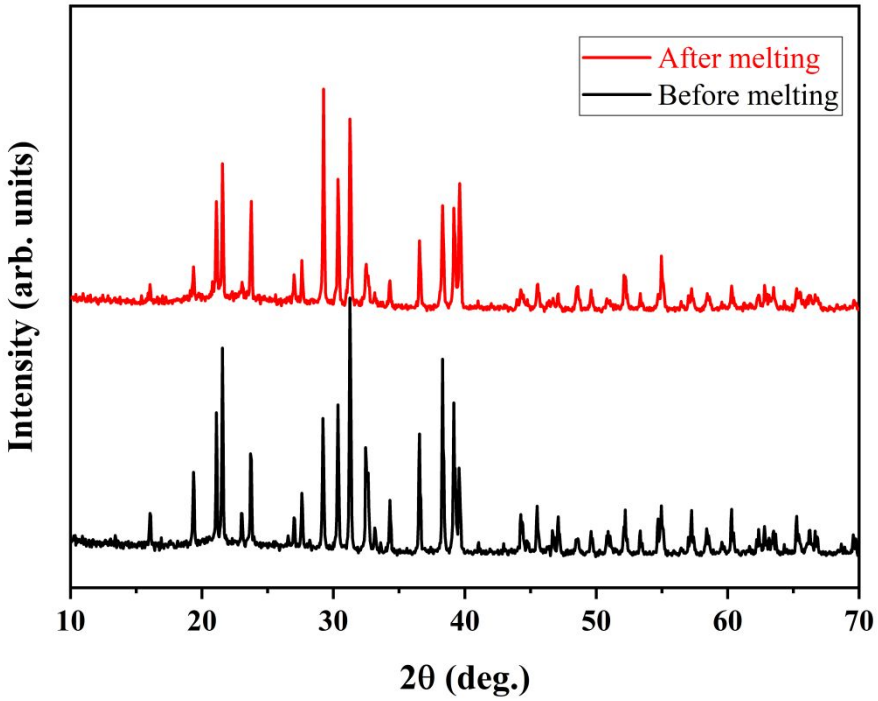

Figure S7. Powder X-ray diffraction patterns of BaCNOBr before and after melting.

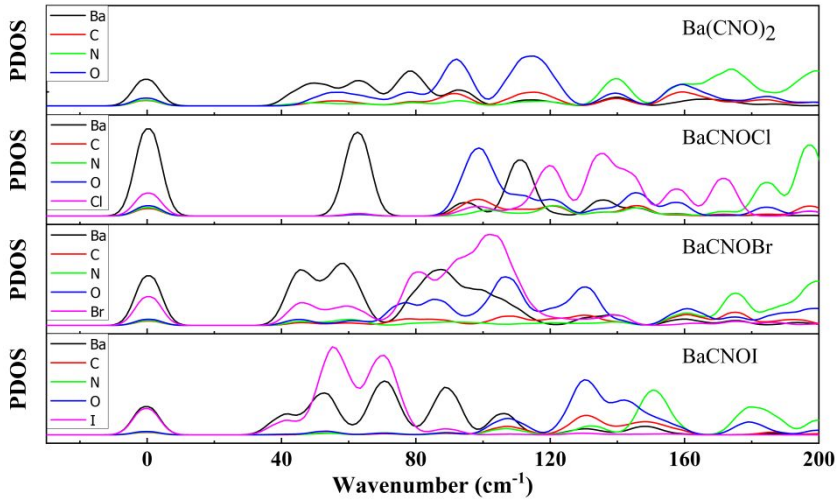

Figure S8. Phonon projected density of states of $Ba(CNO)_2$, BaCNOCl, BaCNOBr and BaCNOI.

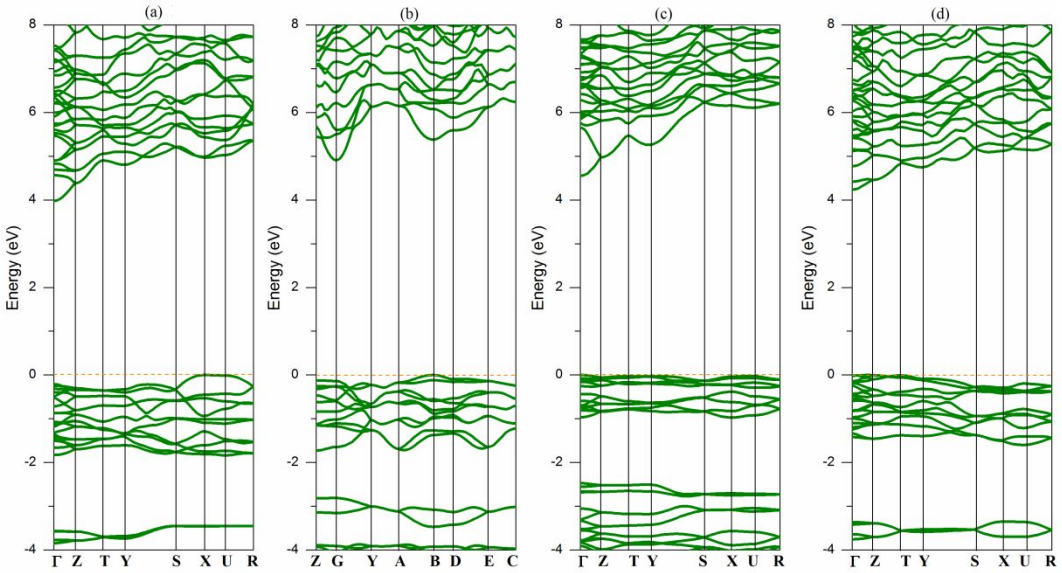

Figure S9. Band structures of (a) $Ba(CNO)_2$, (b) BaCNOCl, (c) BaCNOBr and (d) BaCNOI.

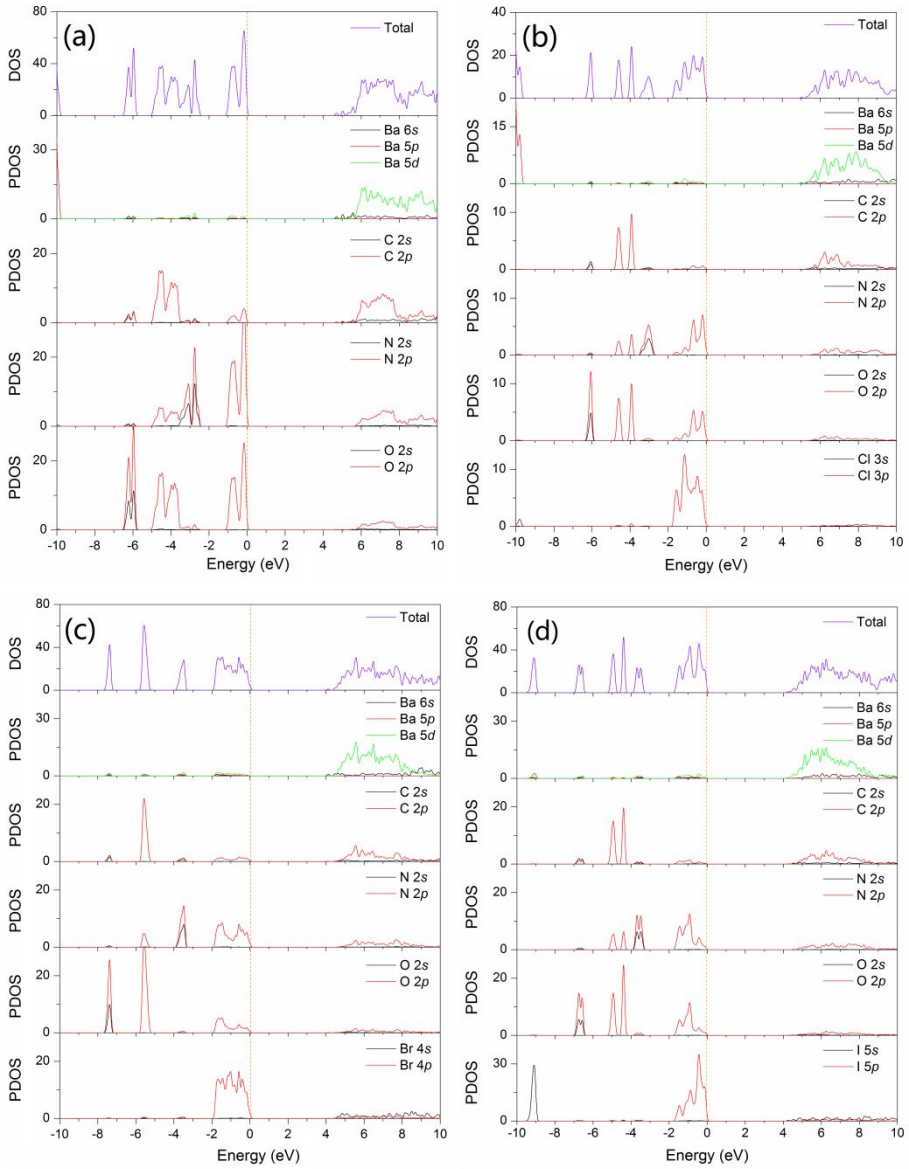

Figure S10. The density of states of (a) $Ba(CNO)_2$, (b) BaCNOCl, (c) BaCNOBr and (d) BaCNOI.

Table S1. Crystal data and structure refinements for BaCNOCl, BaCNOBr, BaCNOI and $Ba(CNO)_2$.

Formula	BaCNOCl	BaCNOBr	BaCNOI	$Ba(CNO)_2$
Weight	214.81	259.27	306.26	358.72
Temperature/K	293(2)	293(2)	293.25(10)	293(2)
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1/m$	*Pnma*	*Pnma*	*Pnma*
a/Å	5.5757(15)	8.2268(5)	8.5754(5)	8.7132(6)
b/Å	4.4925(10)	4.5519(3)	4.7566(3)	4.2901(3)
c/Å	7.850(2)	10.9861(8)	11.5553(7)	11.8029(8)
β/°	102.38(3)	90.00	90	90
Volume/Å^3	192.06(9)	411.40(5)	471.34(5)	441.20(5)
Z	2	4	4	4
ρ_{calc}g/cm^3	3.714	4.186	4.316	3.333
μ/mm^{-1}	10.821	19.167	14.803	17.613
F(000)	188.0	448.0	520.0	616.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.482 to 52.664	6.18 to 52.74	5.916 to 52.714	5.812 to 52.714
Index ranges	-6 ≤ h ≤ 6, -5 ≤ k ≤ 5, -9 ≤ l ≤ 9	-10 ≤ h ≤ 10, -5 ≤ k ≤ 5, -13 ≤ l ≤ 13	-10 ≤ h ≤ 10, -5 ≤ k ≤ 5, -13 ≤ l ≤ 14	-9 ≤ h ≤ 10, -5 ≤ k ≤ 5, -14 ≤ l ≤ 14
Reflections collected	1672	4145	5043	4288
Independent reflections	440 [R_{int} = 0.0478]	476 [R_{int} = 0.0412]	536 [R_{int} = 0.0468]	512 [R_{int} = 0.0430]
Data/restraints/ parameters	440/0/31	476/0/31	536/0/31	512/0/43
Goodness-of-fit on F^2	1.009	1.023	1.131	1.101
Final R indexes [I>=2σ (I)]	R_1 = 0.0258, wR_2 = 0.0543	R_1 = 0.0128, wR_2 = 0.0288	R1 = 0.0273, wR2 = 0.0731	R_1 = 0.0144, wR_2 = 0.0296
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0557	R_1 = 0.0146, wR_2 = 0.0292	R1 = 0.0290, wR2 = 0.0737	R_1 = 0.0156, wR_2 = 0.0300

Table S2. Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for BaCNOCl, BaCNOBr, BaCNOI and $Ba(CNO)_2$. U_{eq} is defined as one third of the trace of the orthogonalised U_{IJ} tensor.

	Atom	x	y	z	U(eq)
BaCNOCl	Ba1	3215.4(8)	2500	7390.5(6)	15.89(18)
	C1	1594(15)	2500	1372(10)	18.5(16)
	O1	9455(10)	2500	1520(8)	25.5(13)
	N1	3643(12)	2500	1167(9)	20.3(14)
	Cl1	7639(3)	2500	5515(2)	18.6(4)
BaCNOBr	Ba1	2302.6(3)	2500	5836.6(2)	12.34(11)
	C1	668(5)	2500	2966(4)	12.8(8)
	O1	1441(4)	2500	2017(3)	19.2(7)
	N1	4936(4)	2500	1127(3)	16.7(8)
	Br1	6429.0(5)	2500	6164.3(4)	17.61(13)
BaCNOI	Ba1	2269.7(7)	2500	3419.3(5)	22.2(2)
	C1	1132(8)	2500	438(6)	1.2(13)
	O1	6866(11)	2500	5477(8)	41(2)
	N1	534(11)	2500	1341(9)	33(2)
	I1	939.1(8)	2500	6428.2(6)	25.3(2)
$Ba(CNO)_2$	Ba1	1886.2(3)	2500	3880.0(2)	11.63(9)
	C1	946(5)	2500	934(3)	15.3(9)
	C2	1284(5)	2500	6745(3)	14.1(8)
	O1	87(3)	2500	1743(3)	22.9(7)
	O2	2307(3)	2500	7450(2)	21.0(7)
	N1	1791(4)	2500	155(3)	20.9(8)
	N2	315(4)	2500	6051(3)	15.4(7)

Table S3. Selected bond lengths (Å) and bond angles (degree) for BaCNOCl.

Ba1-O1[1]	2.922(4)	Ba1-Cl1[5]	3.142(2)
Ba1-O1[2]	2.922(4)	Ba1-Cl1[6]	3.1639(15)
Ba1-N1	2.923(7)	Ba1-Cl1[7]	3.1639(15)
Ba1-N1[3]	2.923(4)	C1-N1	1.187(11)
Ba1-N1[4]	2.923(4)	C1-O1	1.223(10)
Ba1-Cl1	3.132(2)		
N1-C1-O1	177.7(9)		

Symmetry codes: [1]-X,-Y,1-Z; [2]-X,1-Y,1-Z; [3]1-X,1-Y,1-Z; [4]1-X,-Y,1-Z; [5]-1+X,+Y,+Z; [6]1-X,-Y,-Z; [7]1-X,1-Y,-Z;

Table S4. Selected bond lengths (Å) and bond angles (degree) for BaCNOBr.

Ba1-O1	2.8161(17)	Ba1-Br1[1]	3.3319(4)
Ba1-O1[1]	2.8161(17)	Ba1-Br1[5]	3.3722(5)
Ba1-N1[2]	2.906(4)	Ba1-Br1[6]	3.4137(5)
Ba1-N1[3]	2.945(2)	Ba1-C1[2]	3.428(4)
Ba1-N1[4]	2.945(2)	C1-N1	1.164(6)
Ba1-Br1	3.3319(4)	C1-O1	1.221(5)
N1-C1-O1	179.7(4)		

Symmetry codes: [1]+X,1+Y,+Z; [2]3/2-X,1-Y,-1/2+Z; [3]1/2+X,1+Y,3/2-Z; [4]1/2+X,+Y,3/2-Z; 3/2-X,1-Y,1/2+Z; [6]1-X,1-Y,1-Z

Table S5. Selected bond lengths (Å) and bond angles (degree) for BaCNOI.

Ba1-O1	2.799(5)	Ba1-I1[4]	3.6481(7)
Ba1-O1[1]	2.799(5)	Ba1-I1[5]	3.6481(7)
Ba1-N1[2]	2.813(10)	Ba1-I1[6]	3.6594(9)
Ba1-N1[3]	2.825(10)	C1-N1	1.163(13)
Ba1-I1	3.6413(7)	C1-O1	1.230(12)
Ba1-I1[1]	3.6413(7)		
N1-C1-O1	175.4(9)		

Symmetry codes: [1]+X,1+Y,+Z; [2]2-X,1-Y,1-Z; [3]3/2-X,1-Y,-1/2+Z; [4]1/2+X,+Y,1/2-Z; [5]1/2+X,1+Y,1/2-Z; [6]1-X,1-Y,1-Z

Table S6. Selected bond lengths (Å) and bond angles (degree) for $Ba(CNO)_2$.

Ba1-O1	2.8182(18)	Ba1-N1[5]	2.905(3)
Ba1-O1[1]	2.8182(18)	Ba1-O2[6]	2.970(3)
Ba1-N2[1]	2.863(2)	C1-N1	1.177(5)
Ba1-N2	2.863(2)	C1-O1	1.220(5)
Ba1-N1[2]	2.879(2)	C2-N2	1.177(5)
Ba1-N1[3]	2.879(2)	C2-O2	1.214(5)
Ba1-O2[4]	2.884(3)		
N1-C1-O1	178.8(4)	N2-C2-O2	179.4(4)

Symmetry codes: [1]+X,1+Y,+Z; [2]1/2+X,1+Y,1/2-Z; [3]1/2+X,+Y,1/2-Z; [4]1-X,1-Y,1-Z; [5]3/2-X,1-Y,1/2+Z; [6]3/2-X,1-Y,-1/2+Z