Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$A_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$ ($A = Ca^{2+}$, Sr^{2+}) iso-cyamelurates with ultra-large π-conjugated group and excellent nonlinear optical properties

Xiaoguang Du,[a] Fangyan Wang,[b] Fei Liang,[b,] Zhanggui Hu,[a] Yicheng Wu,[a,b] Xinyuan Zhang [a,*]*

[a] Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystals, Tianjin University of Technology, Tianjin 300384, China.
[b] State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, China.

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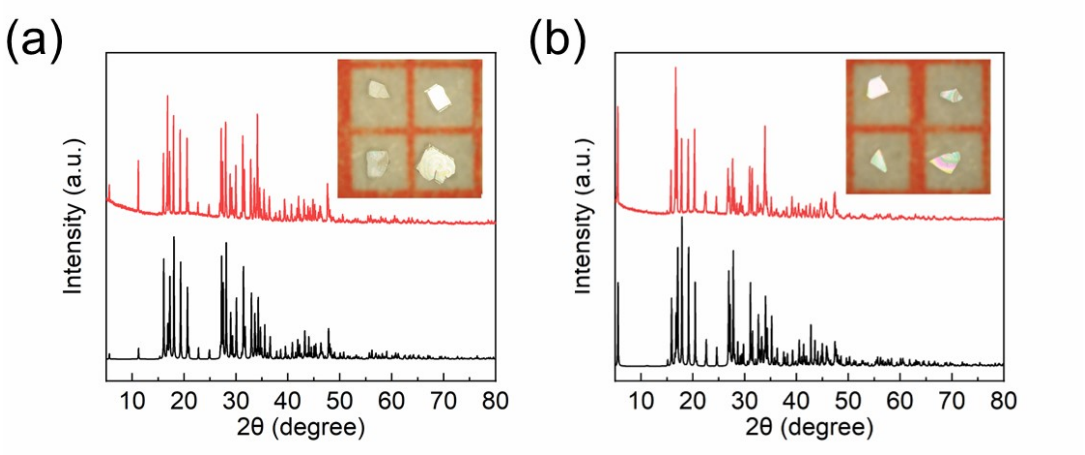

Figure S1. Powder X-ray diffraction pattern of (a) $Ca_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$ and (b) $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

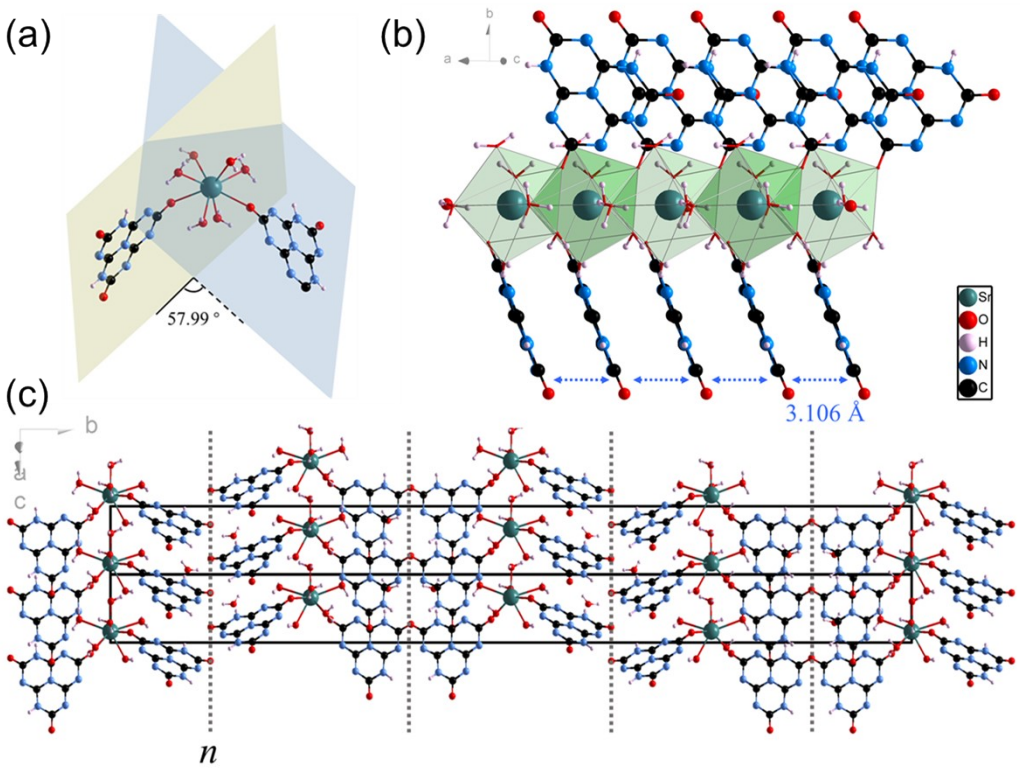

Figure S2. Crystal structure of $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$ (**II**). (a) The coordination environment of Sr^{2+}; (b) the arrangement of $(H_2C_6N_7O_3)^-$ anions; (c) the packing diagram of $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

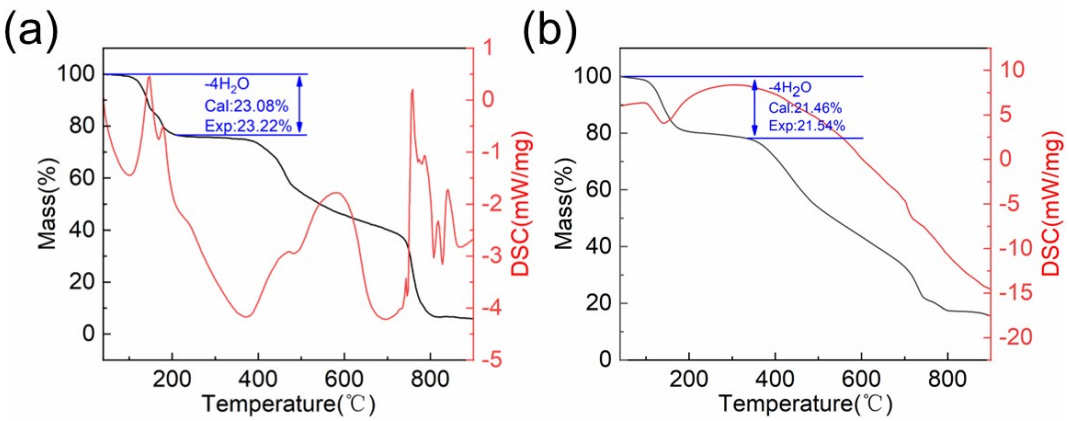

Figure S3. Thermal analysis of (a) $Ca_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$ and (b) $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

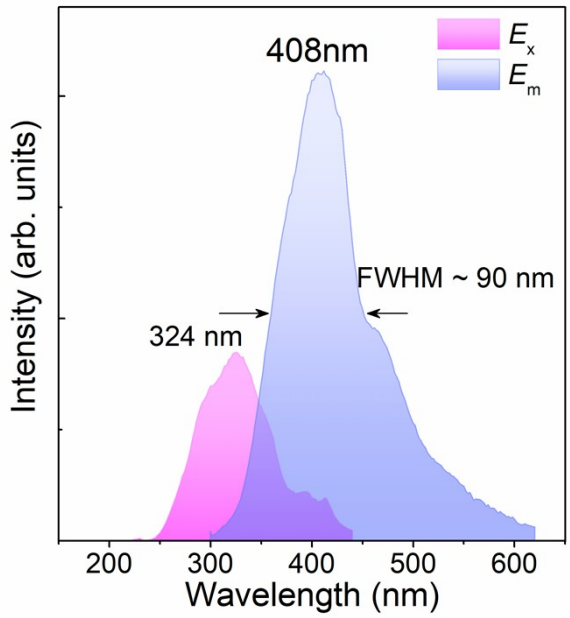

Figure S4. Photoluminescent measurement of $Ca_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

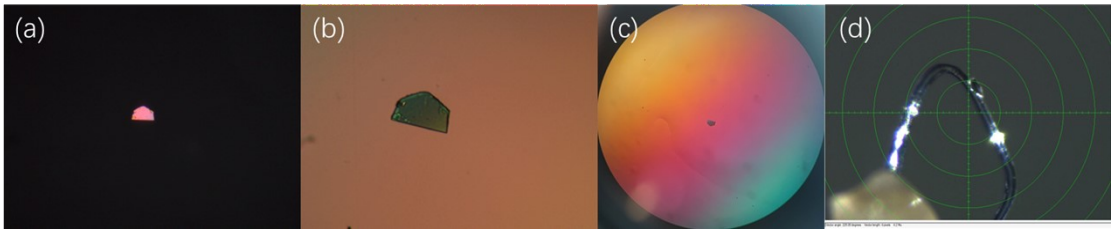

Figure S5. Birefringence measurement of $Ca_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$; (a) the original crystal; (b) the crystal in the extinction state; (c) the crystal interference color observed under the microscope and (d) the photographs of crystal thickness.

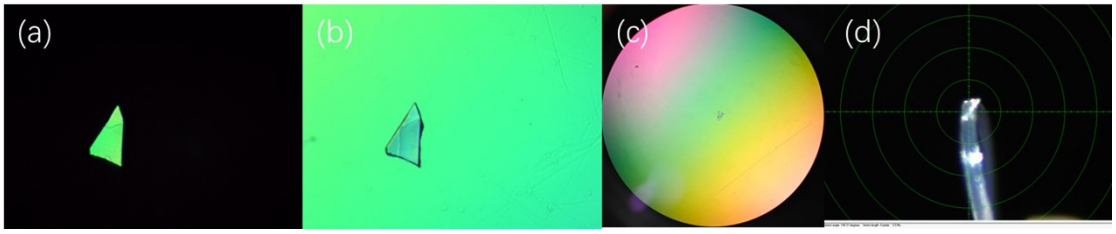

Figure S6. Birefringence measurement of $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$; (a) the original crystal; (b) the crystal in the extinction state; (c) the crystal interference color observed under the microscope and (d) the photographs of crystal thickness.

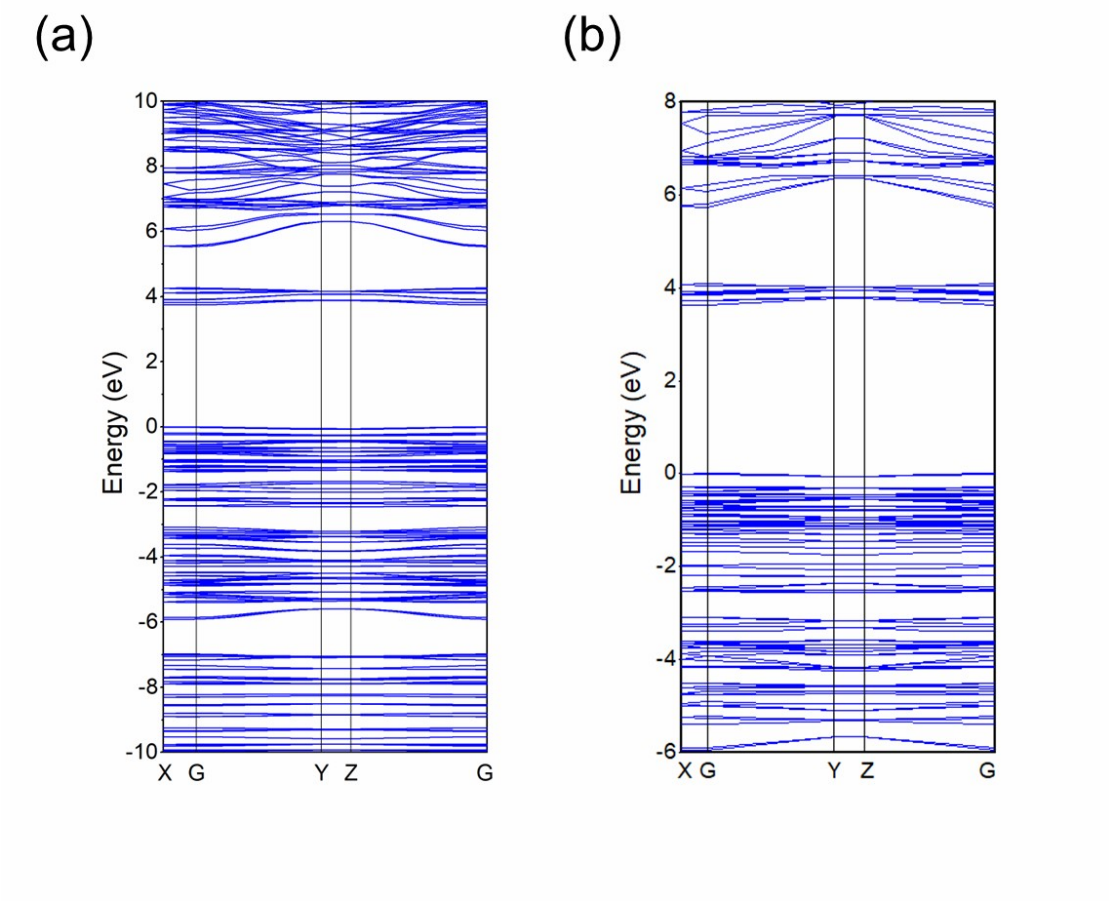

Figure S7. Calculated band structure of (a) $Ca_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$ and (b) $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

Table S1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters($Å^2 \times 10^3$) for $Ca_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

Atom	x	y	z	U (eq) [a]
Ca1	7500	2500	9134(3)	25.6(4)
O1	5961(3)	2743.3(6)	7492(7)	28.0(11)
O5	9003(3)	2494.8(6)	11910(8)	27.3(10)
O7	6676(4)	2318.5(7)	6067(7)	33.3(12)
O6	7634(4)	2874.0(6)	10713(8)	36.7(12)
O2	7686(4)	3747.5(6)	5099(7)	33.2(11)
O4	8623(4)	3462.7(6)	9344(8)	35.6(11)
O3	4074(4)	3228.5(6)	-1910(8)	33.8(11)
N6	7120(4)	3416.0(7)	5972(8)	23.4(12)
N3	6607(4)	3074.7(7)	6834(9)	23.8(12)
N5	5274(4)	3402.5(8)	386(8)	25.2(12)
N2	4656(4)	3055.4(7)	1186(9)	25.6(12)
N4	5932(4)	3236.7(6)	3553(8)	20.1(11)
N1	5331(4)	2891.3(7)	4307(9)	24.5(11)
N7	6452(4)	3591.7(7)	2726(8)	24.0(12)
C4	6560(4)	3235.4(8)	5511(11)	19.7(12)
C6	7103(5)	3593.9(9)	4611(11)	23.9(14)
C1	5960(5)	2897.9(8)	6220(12)	25.1(14)
C3	4632(5)	3223.8(9)	-189(10)	25.2(15)
C5	5898(5)	3417.9(9)	2243(10)	22.2(13)
C2	5296(5)	3058.5(8)	3014(10)	22.5(14)

[a] U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters($Å^2 \times 10^3$) for $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

Atom	x	y	z	U (eq) [a]
Sr1	2500	2500	850(2)	29.6(4)
O1	4042(6)	2748.6(10)	2585(11)	22.0(17)
O4	918(6)	2494.2(9)	-1953(12)	22.4(16)
O2	3355(6)	2313.1(10)	4082(12)	25.7(18)
O7	6380(6)	3463.4(10)	5737(13)	25.4(17)
O5	5902(7)	3233(1)	11962(13)	24.9(17)
O6	2295(6)	3747.7(10)	5012(12)	25.8(18)
N1	4646(7)	2896.7(11)	5749(16)	19.6(18)
N4	4054(7)	3241.8(11)	6506(13)	11.6(18)
O3	2643(7)	2110.4(12)	-728(14)	32.4(19)
N5	2888(7)	3402.1(11)	4120(14)	20(2)
N6	4701(7)	3405.3(12)	9671(14)	19(2)
N3	5335(8)	3060.4(13)	8870(14)	17(2)
N2	3395(7)	3078.5(11)	3259(15)	18.4(18)
N7	3533(7)	3592.1(12)	7353(14)	19.9(19)
C3	3442(8)	3239.3(14)	4569(17)	16(2)
C2	4704(9)	3062.2(15)	7047(17)	15(2)
C1	4021(8)	2902.0(15)	3843(18)	19(2)
C6	2871(8)	3593.4(15)	5478(18)	18(2)
C4	5358(9)	3228.0(14)	10224(15)	16(2)
C5	4091(9)	3419.8(14)	7798(16)	18(2)

[a] U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

Table S3. Anisotropic displacement parameters($Å^2×10^3$) for $Ca_{0.5}H_2C_6N_7O_3·4H_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	28.5(9)	25.8(9)	22.5(9)	0	0	-1.6(8)
O1	32(3)	22(2)	30(3)	9.7(2)	-3(2)	-0.7(19)
O5	29(2)	20(2)	34(3)	5(2)	-3(2)	-1.8(19)
O7	45(3)	24(2)	31(3)	6(2)	-9(2)	-10(2)
O6	30(2)	42(3)	38(3)	-3(2)	-5(2)	1(2)
O2	44(3)	20(2)	36(3)	-3(2)	-3(2)	-11(2)
O4	48(3)	27(2)	32(3)	0(2)	-10(2)	1(2)
O3	42(3)	33(2)	26(3)	2(2)	-13(2)	-3(2)
N6	29(3)	19(2)	22(3)	-1(2)	-7(2)	-3(2)
N3	24(3)	17(3)	30(3)	0(2)	-8(3)	0.5(19)
N5	33(3)	22(3)	21(3)	3(2)	-4(2)	-3(2)
N2	30(3)	21(3)	26(3)	0(2)	-5(2)	-4(2)
N4	24(3)	18(2)	19(3)	-2(2)	-2(2)	-1(2)
N1	27(3)	20(3)	26(3)	4(2)	-8(3)	-3(2)
N7	29(3)	21(3)	21(3)	0(2)	-2(2)	-6(2)
C4	20(3)	16(3)	23(3)	1(3)	-1(3)	2(2)
C6	28(3)	17(3)	27(4)	-3(3)	3(3)	1(2)
C1	26(3)	18(3)	32(4)	1(3)	-2(3)	1(3)
C3	29(3)	22(3)	26(4)	-3(3)	-2(3)	2(3)
C5	26(3)	19(3)	22(3)	2(2)	3(3)	1(2)
C2	28(3)	14(3)	16(3)	-4(3)	0(3)	0(2)

Table S4. Anisotropic displacement parameters($Å^2×10^3$) for $Sr_{0.5}H_2C_6N_7O_3·4H_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr1	32.2(8)	30.4(7)	26.3(7)	0	0	-0.6(8)
O1	26(4)	17(3)	23(4)	-12(3)	-3(3)	5(3)
O4	21(4)	20(3)	25(4)	-6(3)	1(3)	3(3)
O2	28(4)	22(4)	27(4)	-2(3)	-2(3)	8(3)
O7	35(4)	19(3)	22(4)	-2(4)	-10(4)	1(3)
O5	39(5)	28(4)	18(4)	-3(3)	-12(3)	4(4)
O6	33(5)	15(3)	30(4)	7(3)	0(3)	13(3)
N1	26(5)	13(4)	20(4)	-4(4)	-5(4)	5(3)
N4	10(4)	10(4)	14(4)	-1(3)	-4(3)	3(3)
O3	32(5)	34(4)	31(5)	2(4)	16(4)	-2(4)
N5	27(5)	15(4)	17(5)	2(4)	-10(4)	4(4)
N6	31(5)	14(4)	13(4)	-5(3)	-6(4)	7(4)
N3	21(5)	14(4)	17(5)	0(3)	-4(4)	3(3)
N2	23(5)	17(4)	15(4)	-4(4)	-3(4)	0(3)
N7	23(5)	18(4)	19(4)	1(4)	-3(4)	4(4)
C3	13(5)	19(5)	17(5)	4(4)	2(4)	-3(4)
C2	16(5)	15(5)	13(5)	3(4)	7(4)	0(4)
C1	10(5)	19(5)	30(6)	4(5)	-3(4)	1(4)
C6	13(5)	19(5)	23(6)	3(4)	2(4)	1(4)
C4	18(5)	15(5)	13(5)	-2(4)	-1(4)	2(4)
C5	22(6)	14(5)	19(5)	-1(4)	2(4)	0(4)

Table S5. Selected bond lengths for $Ca_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

Bond	Length (Å)	Bond	Length (Å)
Ca1-O1[1]	2.566(4)	N3-C4	1.287(7)
Ca1-O1	2.566(4)	N3-C1	1.397(7)
Ca1-O5[1]	2.424(4)	N5-C3	1.399(7)
Ca1-O5	2.424(4)	N5-C5	1.334(7)
Ca1-O7[1]	2.368(5)	N2-C3	1.343(7)
Ca1-O7	2.368(5)	N2-C2	1.327(8)
Ca1-O6[1]	2.544(4)	N4-C4	1.384(7)
Ca1-O6	2.544(4)	N4-C5	1.385(7)
O1-C1	1.236(7)	N4-C2	1.387(7)
O2-C6	1.221(6)	N1-C1	1.363(8)
O3-C6	1.220(7)	N1-C2	1.308(7)
N6-C4	1.343(7)	N7-C6	1.362(8)
N6-C6	1.385(7)	N7-C5	1.306(7)

[1]3/2-X, 1/2-Y, +Z

Table S6. Selected bond lengths for $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

Bond	Length (Å)	Bond	Length (Å)
Sr1-O1[1]	2.635(7)	N4-C3	1.376(12)
Sr1-O1	2.635(7)	N4-C2	1.414(12)
Sr1-O4[1]	2.529(7)	N4-C5	1.373(11)
Sr1-O4	2.529(7)	N5-C3	1.350(12)
Sr1-O2[1]	2.497(7)	N5-C6	1.370(13)
Sr1-O2	2.497(7)	N6-C4	1.410(12)
Sr1-O3[1]	2.653(8)	N6-C5	1.345(13)
Sr1-O3	2.653(8)	N3-C2	1.331(13)
O1-C1	1.234(11)	N3-C4	1.340(12)
O5-C4	1.232(12)	N2-C3	1.291(12)
O6-C6	1.227(11)	N2-C1	1.390(12)
N1-C2	1.311(13)	N7-C6	1.377(13)
N1-C1	1.368(14)	N7-C5	1.306(12)

[1]1/2-X, 1/2-Y, +Z

Table S7. Selected bond angles for $Ca_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

Angle	(°)	Angle	(°)
O1[1]-Ca1-O1	135.0(2)	C1-O1-Ca1	135.0(4)
O5-Ca1-O1	141.59(13)	C4-N6-C6	123.9(5)
O5[1]-Ca1-O1[1]	74.95(14)	C5-N5-C3	124.1(5)
O5[1]-Ca1-O5	93.5(2)	C2-N2- C3	120.3(5)
O5-Ca1-O6[1]	77.18(14)	O2-C6-N6	119.6(6)
O5-Ca1-O6	73.33(13)	O1-C1-N3	117.8(6)
O7-Ca1-O1[1]	72.76(15)	O3-C3-N5	118.6(5)
O7[1]-Ca1-O1[1]	72.80(15)	N6-C4-N4	115.5(5)
O7-Ca1-O5	145.25(14)	N3-C4-N6	121.3(5)
O7-Ca1-O5	103.82(16)	N7-C6-N6	119.0(5)
O7[1]-Ca1-O7[1]	78.5(2)	N1-C1-N3	122.7(5)
O7-Ca1-O6	139.49(15)	N2-C3-N5	118.3(5)
O7-Ca1-O6[1]	79.32(15)	N5-C5-N4	115.2(5)
O6[1]-Ca1-O1[1]	68.42(13)	N7-C5-N5	121.3(5)
O6-Ca1-O1[1]	130.68(13)	C2-N1-C1	119.2(5)
O6[1]-Ca1-O6	136.4(2)	O2-C6-N7	121.4(5)

[1]3/2-X, 1/2-Y, +Z

Table S8. Selected bond angles for $Sr_{0.5}H_2C_6N_7O_3 \cdot 4H_2O$.

Angle	(°)	Angle	(°)
O1[1]-Sr1-O1	133.2(3)	C1-O1-Sr1	134.6(7)
O1-Sr1-O3	130.9(2)	C2-N1-C1	120.6(8)
O1[1]-Sr1-O3	68.3 (2)	C3-N4-C2	118.4(8)
O4[1]-Sr1-O1	74.8(2)	C5-N4-C2	121.0(8)
O4[1]-Sr1-O1[1]	142.36(19)	C3-N5-C6	124.7(9)
O4-Sr1-O3[1]	78.2(2)	C5-N6-C4	123.5(8)
O2-Sr1-O1	72.0(2)	N5-C3-N4	114.8(8)
O2-Sr1-O4[1]	103.0(2)	N2-C3-N4	123.4(9)
O2[1]-Sr1-O4	144.8(2)	N2-C3-N5	121.9(9)
O2-Sr1-O2[1]	77.5(2)	O1-C1-N1	119.0(8)
O2[1]-Sr1-O3[1]	138.4(2)	O1-C1-N2	119.4(9)
O2-Sr1-O3	79.1(2)	N1-C1-N2	121.6(9)
O3-Sr1-O3[1]	138.0(4)	N3-C4-N6	118.5(8)
O2[1]-Sr1-O3[1]	79.1(2)	N6-C5-N4	115.9(8)
O2-Sr1-O3[1]	138.4(2)	C7-C5-N4	123.7(9)
O2[1]-Sr1-O4	103.0(2)	O7-C5-N7	120.3(9)

[1]1/2-X, 1/2-Y, +Z