Supplementary Material (ESI) for Dalton Transactions

Supporting information

$Zn_3(4\text{-}OOCC_6H_4PO_3)_2$: A polar metal phosphonate with pillared layered structure showing SHG-activity and large dielectric anisotropy

Jin-Tang Li,[a] Deng-Ke Cao,[a] Tomoyuki Akutagawa,[b] Li-Min Zheng[a,]*

Experimental.

Methods. The elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. The powder XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer. Approximate estimations of second-order-nonlinear optical intensity were obtained by comparison of the results obtained from a powder sample (80±150 mm diameter) in the form of a pellet (Kurtz powder test[11]) with those obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward-scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation.

Temperature dependent anisotropic dielectric measurements. Temperature-dependent dielectric constants were measured by the two-probe AC impedance method at the frequencies from 1 to 1000 kHz (HP4194A). A single crystal (dimension: 1.5 x 1.0 x 0.7 mm^3) was placed into a cryogenic refrigerating system (Daikin PS24SS). The electrical contacts were prepared using gold paste (Tokuriki 8560) to attach the 10-μm ϕ gold wires to the single crystal.

Table S1 Selected bond lengths [Å] and angles [°] for **1**

Zn1-O1	2.040(6)	Zn1-O5C	1.985(7)
Zn1-O3	2.367(7)	Zn1-O6B	1.980(6)
Zn1-O10A	1.909(7)	Zn2-O8D	1.883(6)
Zn2-O2	1.921(6)	Zn2-O4E	1.921(7)
Zn2-O6	1.981(6)	Zn3-O7G	1.941(6)
Zn3-O3	1.981(6)	Zn3-O9A	1.948(7)
Zn3-O1F	2.028(6)	P1-O1	1.550(6)
P1-O2	1.483(7)	P1-O3	1.533(7)
P2-O6	1.556(6)	P2-O8	1.515(6)
P2-O7	1.496(7)	C7-O4	1.252(12)
C7-O5	1.238(13)	C14-O9	1.232(12)
C14-O10	1.240(12)		
O1-Zn1-O3	66.2(2)	P1-O2-Zn2	149.0(5)
O5C-Zn1-O1	92.0(3)	P2-O6-Zn2	127.9(4)
O6B-Zn1-O1	117.3(3)	P2-O8-Zn2K	132.0(4)
O10A-Zn1-O1	123.8(3)	C7-O4-Zn2H	119.0(6)
O5C-Zn1-O3	153.7(3)	O8D-Zn2-O4E	121.3(3)
O6B-Zn1-O3	98.6(2)	O8D-Zn2-Zn1F	152.5(2)
O10A-Zn1-O3	89.7(3)	O7G-Zn3-O3	115.1(3)
O6B-Zn1-O5C	104.8(3)	O9A-Zn3-O3	111.8(3)
O10A-Zn1-O5C	90.7(3)	O3-Zn3-O1F	113.8(3)
O10A-Zn1-O6B	116.1(3)	O7G-Zn3-O1F	99.2(3)
P1-O1-Zn1	101.1(3)	O9A-Zn3-O1F	113.3(3)
P1-O3-Zn1	88.6(3)	O7G-Zn3-O9A	102.5(3)
P2-O6-Zn1F	127.5(4)	P1-O3-Zn3	131.6(4)
C7-O5-Zn1I	131.4(7)	P1-O1-Zn3B	129.9(3)
C14-O10-Zn1L	150.3(7)	P2-O7-Zn3J	151.1(5)
O2-Zn2-O6	92.2(3)	C14-O9-Zn3L	125.8(7)
O4E-Zn2-O2	104.5(3)	Zn3-O3-Zn1	112.6(3)
O8D-Zn2-O2	110.9(3)	Zn1F-O6-Zn2	104.0(3)
O4E-Zn2-O6	109.1(3)	Zn3B-O1-Zn1	128.9(3)
O8D-Zn2-O6	114.5(3)		

Symmetry codes: A: -x+2, -y+1, z-1/2; B: x-1/2, -y+1, z; C: -x+1, -y+1, z-1/2; D: x-1/2, -y+2, z; E: -x+3/2, y, z-1/2; F: x+1/2, -y+1, z; G: x, y-1, z; H: -x+3/2, y, z+1/2; I: -x+1, -y+1, z+1/2; J: x, y+1, z; K: x+1/2, -y+2, z; L: -x+2, -y+1, z+1/2.

Table S2. Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms

Atom	x	y	z	U(eq)
Zn1	0.87769(7)	1.32017(8)	0.60037(3)	0.0184(2)
Zn2	0.63833(6)	0.85888(7)	0.57733(3)	0.0168(2)
Zn3	1.03307(7)	0.69438(7)	0.56020(3)	0.0166(2)
P1	0.87853(16)	1.01318(18)	0.50623(8)	0.0149(5)
P2	0.73965(16)	0.53790(17)	1.01096(8)	0.0147(5)
O1	0.6495(5)	0.8190(5)	0.6797(2)	0.0290(16)
O2	0.5103(4)	0.6229(5)	0.6741(2)	0.0287(16)
O3	0.6094(4)	0.5325(4)	1.05302(18)	0.0163(12)
O4	0.7964(4)	0.3742(4)	1.02220(19)	0.0170(12)
O5	0.8316(4)	0.6598(4)	1.0343(2)	0.0237(16)
O6	0.9501(4)	1.2193(5)	0.1571(2)	0.0310(16)
O7	0.7440(5)	1.2716(6)	0.1757(2)	0.049(2)
O8	0.7405(4)	1.0135(4)	0.53439(19)	0.0203(12)
O9	0.9532(4)	1.1402(4)	0.54940(18)	0.0147(12)
O10	0.9508(4)	0.8621(4)	0.5083(2)	0.0197(14)
C1	0.5941(6)	0.7018(7)	0.7046(3)	0.022(2)
C2	0.6324(6)	0.6534(7)	0.7797(3)	0.019(2)
C3	0.5571(7)	0.5497(7)	0.8171(3)	0.024(2)
C4	0.5912(6)	0.5113(7)	0.8871(3)	0.023(2)
C5	0.6991(6)	0.5760(6)	0.9190(3)	0.0143(17)
C6	0.7732(7)	0.6801(7)	0.8805(3)	0.026(2)
C7	0.7397(8)	0.7196(8)	0.8109(3)	0.030(2)
C8	0.8501(7)	1.2219(7)	0.1945(3)	0.023(2)
C9	0.8595(7)	1.1640(7)	0.2705(3)	0.018(2)
C10	0.7606(7)	1.2019(6)	0.3176(3)	0.0200(17)
C11	0.7674(6)	1.1593(6)	0.3894(3)	0.018(2)

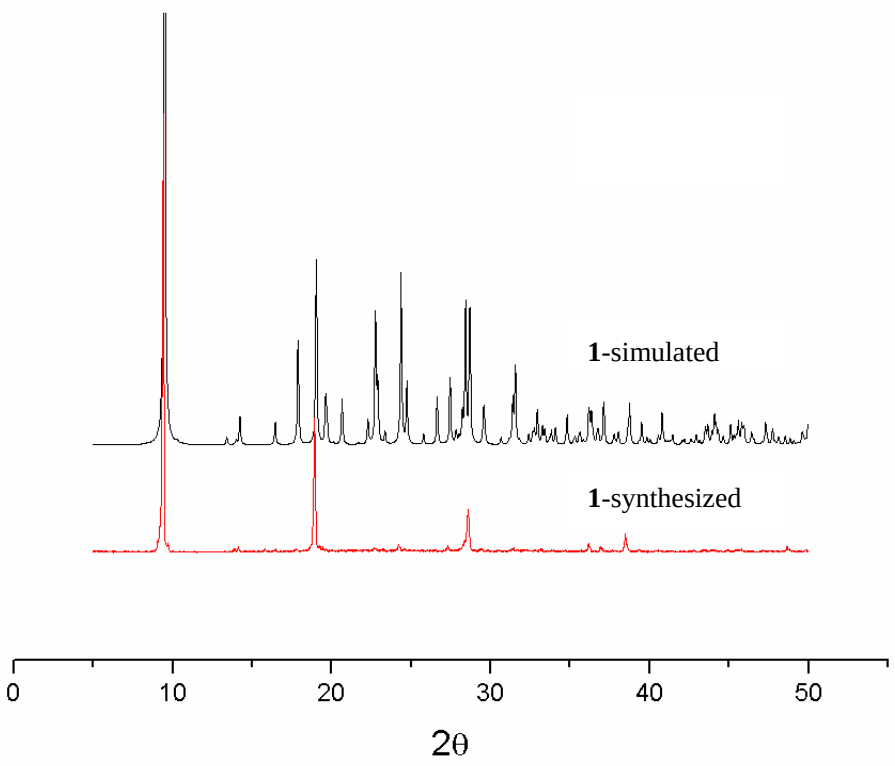

Fig. S1. The XRD patterns for compound **1**

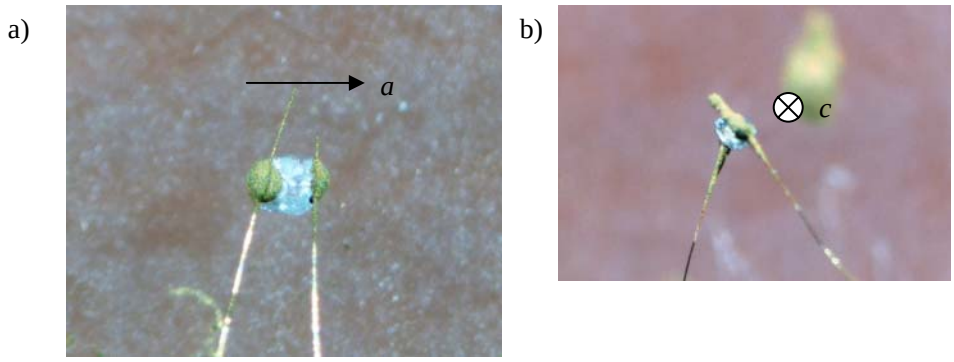

Fig. S2. Crystal - electrode configuration of dielectric measurements along the a) *a*- and b) *c*-axis.