

Supplementary Information

The First Example of Molecule-based Ferroelectric with Barium Element:

Catena-(μ_2 -nitrito-O,O)-bi-aqua-(18-crown-6)-barium nitrite

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All reagents and solvents in the syntheses were of reagent grade and were used without further purification. Powder X-ray diffraction (PXRD) was measured on a Rigaku D/MAX 2000 PC X-Ray Diffraction instrument. X-ray diffraction was carried out using a Rigaku CCD diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at various temperatures. The structure was solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXL97 software package (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically. For dielectric measurements, the single-crystals were cut into thin plate perpendicular to the polarization axes. Silver conduction paste deposited on the surfaces was used as the electrodes. Complex dielectric permittivity was measured with an Tonghui TH2828 impedance analyzer. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21. Specific heat analyses were carried out on a Quantum Design PPMS. For Second Harmonic Generation (SHG) measurement, an unexpanded laser beam with low divergence (pulsed Nd:YAG at a wavelength of 1064 nm) was used. The numerical values of the nonlinear optical coefficients for SHG have been determined by comparison with a KDP reference^{S1}.

S1. D.-W. Fu, W. Zhang, H.-L. Cai, J.-Z. Ge, Y. Zhang and R.-G. Xiong, *Adv. Mater.*, 2011, **23**, 5658

Table S1. Selected bond lengths (Å) and angles (°) for PP.

O(1)-Ba(1)	2.889(5)	O(4)-Ba(1)	2.846(7)
O(2)-Ba(1)	2.862(5)	O(3)-Ba(1)	2.895(7)
O(6)-Ba(1)	2.797(6)	O(1W)-Ba(1)	2.791(6)
Ba(1)-O(1W)#1	2.791(6)	Ba(1)-O(5)#3	2.857(8)
Ba(1)-O(2)#1	2.862(5)	Ba(1)-O(3)#1	2.895(7)
O(5)-Ba(1)#4	2.857(8)	N(1)-O(5)	1.221(1)
N(2)-O(8)	0.957(4)	N(2)-O(8)#2	0.957(4)
N(2)-O(7)#2	1.254(5)	N(2)-O(7)	1.254(5)
O(8)-N(2)-O(8)#2	180(3)	O(8)-N(2)-O(7)#2	51.5(4)
O(8)#2-N(2)-O(7)#2	128.5(4)	O(8)-N(2)-O(7)	128.5(4)
O(8)#2-N(2)-O(7)	51.5(4)	O(7)#2-N(2)-O(7)	180.0(4)
O(1W)-Ba(1)-O(1W)#1	70.0(4)	O(1W)-Ba(1)-O(6)	140.61(6)
O(1W)-Ba(1)-O(4)	117.1(2)	O(6)-Ba(1)-O(4)	75.5(2)
O(6)-Ba(1)-O(5)#3	139.5(2)	O(1W)-Ba(1)-O(2)	127.0(2)
O(6)-Ba(1)-O(2)	69.83(3)	O(4)-Ba(1)-O(2)	91.44(5)
O(1W)-Ba(1)-O(3)	141.44(18)	O(4)-Ba(1)-O(3)	58.72(16)
O(1)-Ba(1)-O(3)	115.2(3)	O(3)-Ba(1)-O(3)#1	116.5(3)

Symmetry code: #1 x, -y+1/2, z; #2 -x, -y, -z+1; #3 x, y, z-1; #4 x, y, z+1.

Table S2. Selected bond lengths (Å) and angles (°) for FP.

Ba(2)-O(4W)	2.759(3)	Ba(2)-O(14)	2.775(3)
Ba(2)-O(3W)	2.799(3)	Ba(2)-O(8)	2.862(3)
Ba(2)-O(16)	2.863(3)	Ba(2)-O(7)	2.864(3)

Ba(2)-O(10)	2.865(3)	Ba(2)-O(12)	2.871(3)
Ba(2)-O(11)	2.884(3)	Ba(2)-O(9)	2.891(3)
Ba(4)-O(1W)	2.773(3)	Ba(4)-O(15)	2.778(3)
Ba(4)-O(2W)	2.815(3)	Ba(4)-O(6)	2.836(3)
Ba(4)-O(1)	2.843(3)	Ba(4)-O(2)	2.845(3)
Ba(4)-O(13)	2.863(3)	Ba(4)-O(4)	2.894(3)
Ba(4)-O(3)	2.896(3)	Ba(4)-O(5)	2.918(3)
Ba(1)-O(7W)	2.740(3)	Ba(1)-O(29)	2.786(3)
Ba(1)-O(8W)	2.793(3)	Ba(1)-O(28)	2.853(3)
Ba(1)-O(32)	2.870(3)	Ba(1)-O(24)	2.874(3)
Ba(3)-O(22)	2.865(3)	Ba(3)-O(30)	2.864(3)
Ba(3)-O(18)	2.880(3)	Ba(3)-O(21)	2.878(3)
Ba(3)-O(17)	2.908(3)	Ba(3)-O(19)	2.913(3)
O(29)-N(3)	1.265(5)	O(30)-N(3)	1.230(4)
O(13)-N(1)	1.247(4)	O(14)-N(1)	1.261(5)
O(15)-N(2)	1.262(5)	O(16)-N(2)	1.243(4)
O(32)-N(4)	1.234(4)	O(31)-N(4)	1.252(5)
O(4W)-Ba(2)-O(14)	139.05(8)	O(4W)-Ba(2)-O(3W)	69.29(9)
O(14)-Ba(2)-O(3W)	141.63(8)	O(4W)-Ba(2)-O(8)	123.20(9)
O(14)-Ba(2)-O(8)	76.04(8)	O(3W)-Ba(2)-O(8)	112.69(9)
O(4W)-Ba(2)-O(16)	69.50(9)	O(14)-Ba(2)-O(16)	139.63(8)
O(3W)-Ba(2)-O(16)	63.50(9)	O(8)-Ba(2)-O(16)	63.64(8)

N(1)-O(13)-Ba(4)	139.7(3)	N(2)-O(15)-Ba(4)	122.0(2)
O(36)-N(6)-O(35)	114.9(3)	O(34)-N(5)-O(33)	114.3(3)
O(40)-N(8)-O(39)	115.6(3)	O(38)-N(7)-O(37)	114.6(3)
