# Supporting Information

## Room-temperature optic-electric duple bistabilities induced by plastic transition

Wei-Jian Xu, Ying Zeng, Wei Yuan, Rong-Guan Qiu, Wei-Xiong Zhang\*, Xiao-Ming Chen

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou, 510275, P. R. China.

#### **Experimental Section**

#### Synthesis

Caution! Although our samples never exploded during handing, perchlorates are potentially explosive. It should be handled with great caution.

All chemicals were commercially available and were used without further purification. The colorless crystals were obtained by slow evaporation of the aqueous solution containing equal molar of acetamidine hydrochloride and acetamidine acetate at room temperature. Yield: 68%. Elemental analysis, calcd (%) for ( $C_2H_7N_2ClO_4$ ): C, 15.15; N, 17.67; H, 4.45. Found: C, 15.70; N, 17.66; H, 4.19.

## X-ray Crystallographic Analyses

The *in situ* variable-temperature single-crystal diffraction experiments were performed on a Rigaku XtaLAB P300DS single-crystal diffractometer, with graphite monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å). The CrystalClear software package was used for data collection, cell refinement and data reduction. Absorption corrections were applied by using multi-scan program REQAB.<sup>[1]</sup> The structures were solved by direct methods and refined using full-matrix least-squares methods with the SHELX program package and Olex2 program.<sup>[2-3]</sup> Non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were generated geometrically. Crystallographic data and structural refinements for **1** are summarized in Table S1. Powder X-ray diffraction (PXRD) patterns were collected on Bruker Advance D8 DAVANCI  $\theta$ -2 $\theta$  diffractometer.

#### **Thermal studies**

Thermogravimetric analyses (TGA) were carried out on a TA Q50 system with a heating rate of 5 K min<sup>-1</sup> under a nitrogen atmosphere. Differential scanning calorimeter (DSC) measurements were performed by heating and cooling the powder samples on a TA DSC Q2000 instrument under a nitrogen atmosphere in aluminium crucibles with heating/cooling rates of 10 K min<sup>-1</sup>.

#### **Dielectric measurement**

The dielectric permittivity measurements for powder samples of 1 were carried on a TH2828A impedance analyser with an applied voltage of 1.0 V, a temperature sweeping rate of approximately 5 K min<sup>-1</sup>, and ac frequency of 8-1000 kHz, respectively.

## **Optical measurement**

Variable-temperature SHG experiments were executed by Kurtz-Perry powder SHG test using an Nd:YAG laser (1064 nm) with input pulse of 350 mV under a programmable cryogenic cooling system.<sup>[4]</sup>



**Figure S1.** The N–H···O hydrogen-bonding interactions of **1**. Symmetric codes: (A) x, y, -1+z; (B) 1+x, y, -1+z; (C)2-x, -1/2+y, 1-z.



Figure S2. Diamond-like supramolecular structure of 1 in crystal phase.



Figure S3. Single crystal of 1 at 298 K (left) and after applying an uniaxial pressure at 350 K (right).



Figure S4. Temperature dependence of the real ( $\epsilon$ ') parts of the dielectric constant of powdered samples of 1 at different frequencies (cooling mode).



**Figure S5.** Temperature dependence of the imaginary ( $\varepsilon''$ ) parts of the dielectric constant of powdered samples of **1** at different frequencies (heating mode).



Figure S6. TGA profile of 1.



Figure S7. PXRD patterns of 1 at room temperature, verifying the purity of the bulk phase.



Figure S8. The variable-temperature PXRD patterns of 1.



Figure S9. Oscilloscope traces of SHG signals of 1 and the referential KDP.

Phase	HT phase	LT phase				
Formula	$C_2H_7N$	C <sub>2</sub> H <sub>7</sub> N <sub>2</sub> ClO <sub>4</sub>				
Formula weight	158	3.55				
Temperature (K)	350(2)	180(2)				
Crystal system	Cubic	Monoclinic				
Space group	$Pm\overline{3}m$	$P2_1$				
a/Å	5.5893(4)	4.8464(1)				
b/Å	5.5893(4)	10.8897(3)				
$c/{ m \AA}$	5.5893(4)	6.0342(1)				
$eta\!$	90	93.671(2)				
$V/\text{\AA}^3$	174.61(4)	317.81(1)				
Ζ	1	2				
$D_{\rm c}/{ m g~cm^{-3}}$	1.508	1.657				
$R_1^a (> 2\sigma)$	0.0583	0.0336				
$wR_2^{b}$ (all data)	0.1304	0.0834				
GOF	1.041	1.132				
Flack	/	0.05(2)				
CCDC number	1820505	1820506				
${}^{a}R_{1} = \sum   F_{o}  -  F_{c}   / \sum  F_{o} , {}^{b}wR_{2} = \{\sum w[(F_{o})^{2} - (F_{c})^{2}]^{2} / \sum w[(F_{o})^{2}]^{2}\}^{1/2}$						

Table S1.Crystal data and structure refinement parameters for 1

Table S2. The parameters of the N–H $\cdots$ O hydrogen-bonding interactions

D	Н	А	$d(D \cdots A)/Å$	∠D–H···A/°
N2	H2D	$O1^{A}$	2.990(4)	166.5
N2	H2E	O4	3.036(4)	175.8
N1	H1A	$O2^{B}$	3.048(4)	149.2
N1	H1B	O3 <sup>C</sup>	3.094(4)	159.3

Symmetry code: (A) +x,+y,-1+z; (B) 1+x,+y,-1+z; (C) 2-x,-1/2+y,1-z.

Compounds	<i>T</i> <sub>c</sub> / K	Times of KDP at "on" state	on/off Contrast	Ref.
(C <sub>6</sub> H <sub>11</sub> NH <sub>3</sub> )(CFCl <sub>2</sub> COO)	150	0.3	12	Ref. 40
NH4((CH3)4N)SO4·H2O	170	1.0	6.3	Ref. 41
(HN <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> )(CF <sub>3</sub> COO)	182	0.8-1.2	35	Ref. 42
[(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> )(18C6)]ClO <sub>4</sub>	214	0.3	7	Ref. 43
(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> [CdCl <sub>3</sub> ]	240	0.4	8	Ref. 44
[(CH <sub>3</sub> ) <sub>3</sub> PCH <sub>2</sub> OH][Cd(SCN) <sub>3</sub> ]	240	0.4	8	Ref. 45
[(CH <sub>2</sub> ) <sub>6</sub> N <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]	280	0.8	25	Ref. 46
(CH <sub>3</sub> C(NH <sub>2</sub> ) <sub>2</sub> )(ClO <sub>4</sub> )	320	1.2	62	This work
2-(hydroxymethyl)-2-nitro-1,3-propanediol	347	2.5	150	Ref. 26
$[(CH_3CH_2)_3(CH_3(CH_2)_2)P][Cd(N(CN)_2)_3]$	386	0.12	40	Ref. 47

Table S3. Typical molecular NLO switch materials

## References

[1] Jacobson, R. REQAB; Molecular Structure Corporation: The Woodlands, Texas, USA, 1998.

[2] Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112.

- [3] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl. Crystallogr. 2009, 42, 339.
- [4] S. K. Kurtz and T. T. Perry, J. Appl. Phys., 1968, 39, 3798.