

# A one-dimensional switchable dielectric material with Pd uptake function: $[(\text{CH}_2)_3\text{NH}_2\text{S}]_2\text{BiCl}_5$

Yu-Ting Liu, Lei He, Ping-Ping Shi, Qiong Ye\* and Da-Wei Fu\*

## EXPERIMENTAL SECTION

### Syntheses

All reagents in this article were analytical reagents and used without further purification.

**1** was obtained through slowly evaporation of the hydrochloric acid solution (about 15 mL) containing thiazolidine (0.8916 g, 10 mmol) and bismuth oxide (2.3298 g, 5 mmol) at room temperature. Colorless transparent ribbon crystals were grown after about one week. The phase purity of **1** was confirmed by powder X-ray diffraction, which matches well with the simulation result of single crystal structure (Fig. S1). In the infrared (IR) spectra of **1** (Fig. S2), several vibration peaks at approximately 3000, 1300 and 700  $\text{cm}^{-1}$  are ascribed to stretching vibration absorption of the C-H, C-N and C-S bond, respectively, indicating the existence of thiazolidine cation in **1**. Furthermore, **1** is non-hygroscopic and can exist stably in the air with a melting point of 459 K. Thermogravimetric analysis (TGA) indicates that **1** begins to decompose at 461 K.

**1-Pd** from treatment of **1** with  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ . Crystal sample **1** (0.5665 g, 1 mmol) was placed into a saturated dichloromethane solution (about 20 mL) of  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  (0.5188 g, 2 mmol). The crystal turned from light white into dark reddish brown within several hours. **1-Pd** was obtained after left it to stand undisturbed for two days at room temperature. Inductively coupled plasma (ICP) elemental analysis revealed the S/Pd ratio of 2.7:1 for the **1-Pd**. IR analysis confirmed the existence of thiazolidine cation in material **1-Pd**. **1-Pd** is also non-hygroscopic and stable in the air with a melting point of 460 K. Moreover, the stability of **1-Pd** was proved by its TGA curve when it is below 461 K.

Treatment of **1** by  $\text{HgCl}_2$ . Crystal sample **1** (0.5665 g, 1 mmol) were placed into a saturated ethanol solution (about 20 mL) of  $\text{HgCl}_2$  (0.5430 g, 2 mmol). **1-Hg** was obtained after left it to

stand undisturbed for two days at room temperature. Inductively coupled plasma (ICP) elemental analysis revealed the S/Hg ratio of 11.3:1 for the **1-Hg**.

### **X-ray Crystallography**

Variable-temperature X-ray single crystal diffraction data of compound **1** were collected on a Rigaku Saturn 924 diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structural data of **1** were collected at 213 K and 363 K. Data were processed by the Crystalclear software package (Rigaku). Variable-temperature crystal structures of **1** were solved by utilizing direct methods and refined by utilizing full-matrix methods based on  $F^2$  through the SHELXLTL software package. All non-H atoms were refined anisotropically and the position of all H atoms were generated geometrically. Crystallographic data and structure refinement details are summarized in Table S1.

CCDC 2009547 and 2009550 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data.request/cif](http://www.ccdc.cam.ac.uk/data.request/cif).

### **Powder X-ray Diffraction**

The powder X-ray diffraction (PXRD) analysis of **1** and **1-Pd** were performed on PANalytical X'Pert PRO X-Ray Diffractometer at 293 K. The diffraction patterns were obtained within  $2\theta$  range of 5–50° with a step size of 0.02°.

### **DSC and TGA Measurements**

Differential scanning calorimetry (DSC) analysis of **1** (18.3 mg) and **1-Pd** (18.5 mg) were performed on Perkin-Elmer Diamond DSC instrument with a heating rate of 10 K/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) of compounds **1** and **1-Pd** were performed on a Netzsch Model TG 209F1 instrument. The measurements were collected in nitrogen flow from 307 K to 1050 K at a rate of 20 K/min, and the result shows that compounds **1** and **1-Pd** begin to decompose at about 461 K (Fig. S3).

### **Dielectric Measurements**

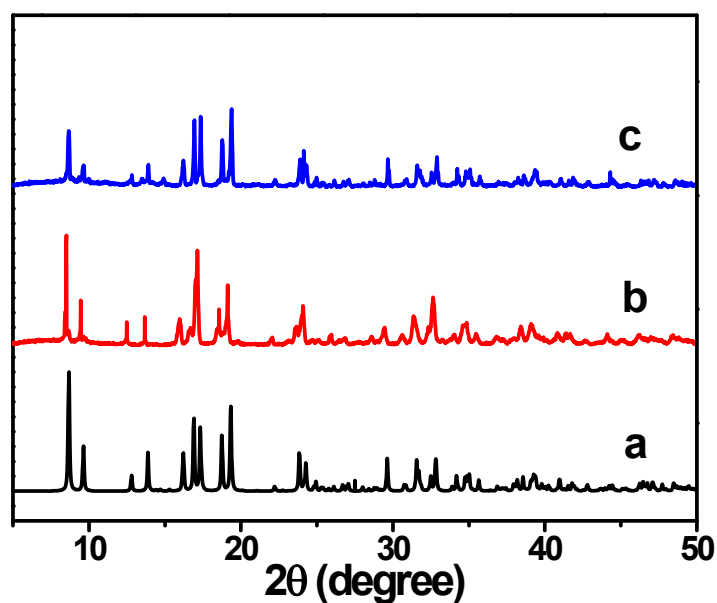
Dielectric constants  $\epsilon'$  and  $\epsilon''$  ( $\epsilon = \epsilon' - i\epsilon''$ , where  $\epsilon'$  and  $\epsilon''$  are the real and imaginary parts, respectively) of **1** and **1-Pd** were tested on a Tonghui TH2828A instrument within the frequency range of 5 kHz to 1 MHz. The powder-pressed pellets with silver painted on both sides were used to measure dielectric constants as the electrodes.

### Ultraviolet–visible (UV–vis) Absorption Spectrum

At room temperature, the UV–vis diffuse reflectance spectrum of **1** and **1–Pd** (polycrystalline samples) were measured on Shimadzu (Tokyo, Japan) UV–2600 spectrophotometer. BaSO<sub>4</sub> was selected as the standard (100%) reflectivity reference.

### Conductivity Measurements

At room temperature, the electrical conductivity values of materials **1**, **1–Pd** and **1–Hg** were measured on ST2722-SD four-terminal powder resistivity tester.



**Fig. S1.** Powder X-ray diffraction patterns at 293 K: a) calculated diffraction pattern from the single-crystal structure of **1**; b) **1**; c) **1–Pd**.

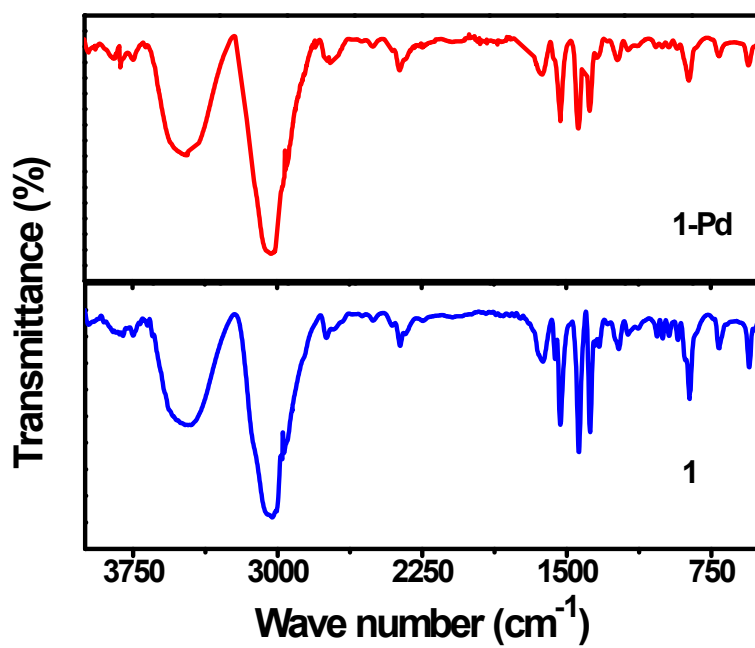


Fig. S2 IR spectrums of **1** and **1-Pd**.

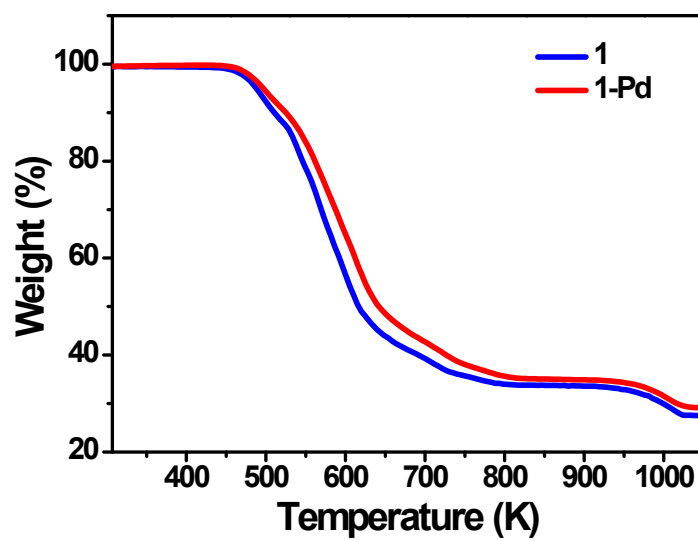
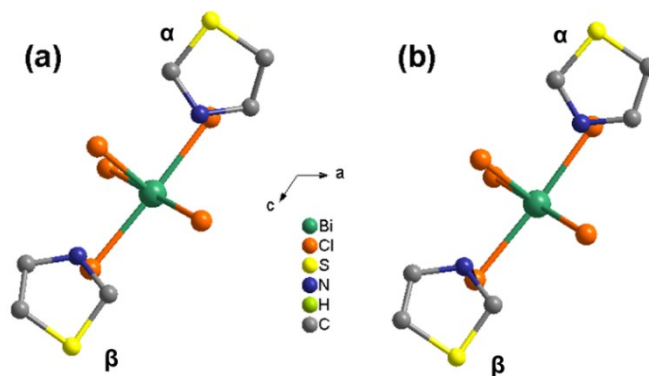
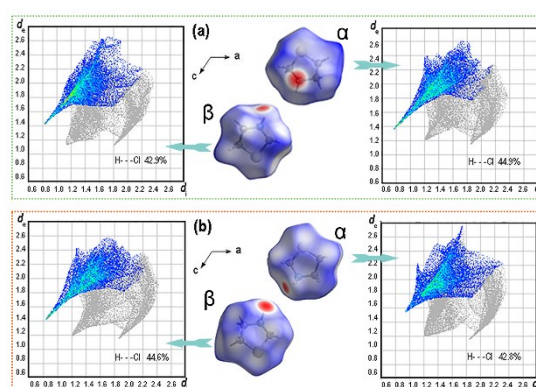


Fig. S3 Thermogravimetric analysis (TGA) plots of **1** and **1-Pd**.



**Fig. S4** The minimum asymmetric unit of **1** at (1) LTP and (2) HTP.



**Fig. S5** The Hirshfeld  $d_{\text{norm}}$  surfaces and the 2D fingerprint plots of the thiazolidine cations in (a) LTP and (b) HTP.



**Fig. S6** Photo images of the crystals: a) **1**; b) **1-Pd**.

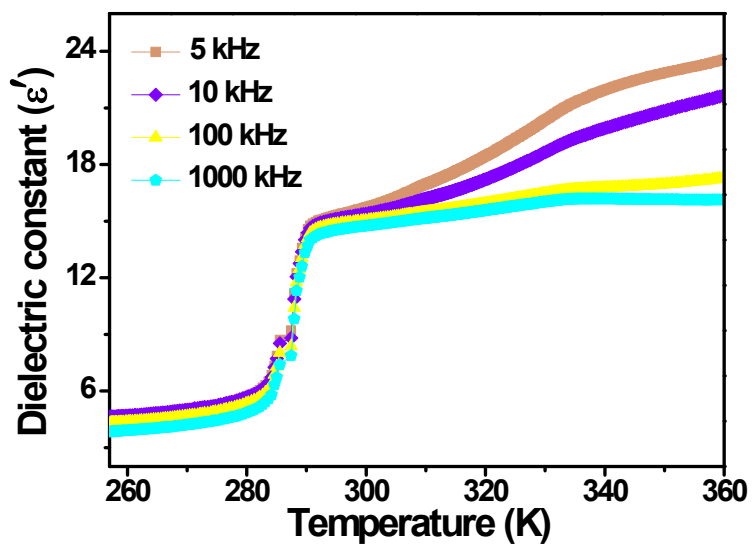


Fig. S7 Dielectric constants ( $\epsilon'$ ) of **1** at 5 kHz, 10 kHz, 100 kHz, and 1000 kHz upon heating.

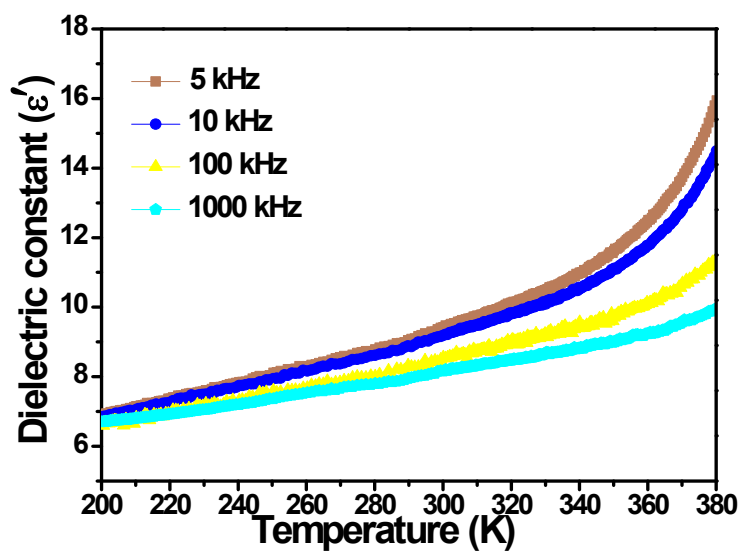


Fig. S8 Dielectric constants ( $\epsilon'$ ) of **1-Pd** at 5 kHz, 10 kHz, 100 kHz, and 1000 kHz upon heating.

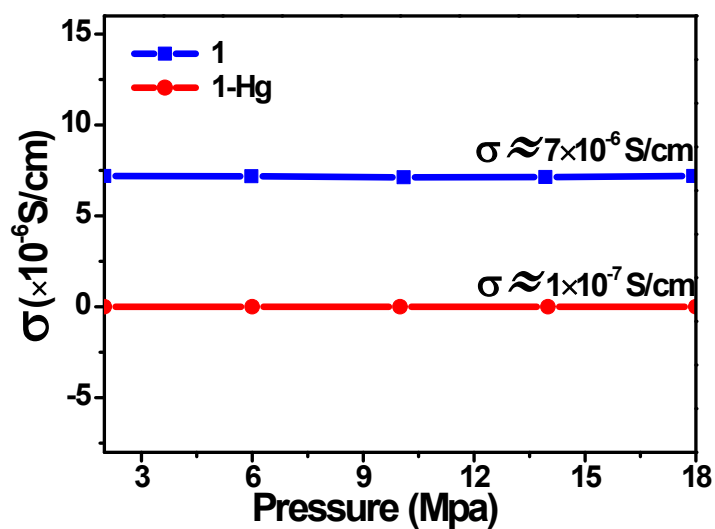


Fig. S9 The electrical conductivity of **1** and **1-Hg**.

**Table S1.** Crystal Data and Structure Refinement Details of sample **1**.

Chemical Formula	[(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> S] <sub>2</sub> BiCl <sub>5</sub>	
<i>T</i> (K)	213 K	363 K
Formula weight	566.56	566.56
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	12.1998(5)	12.2320(4)
<i>b</i> /Å	7.4008(3)	7.5245(2)
<i>c</i> /Å	21.8754(10)	22.0936(8)
<i>α</i> (deg)	90	90
<i>β</i> (deg)	123.518(3)	123.339(2)
<i>γ</i> (deg)	90	90
<i>V</i> /Å <sup>3</sup>	1646.66(13)	1698.84(10)
<i>Z</i>	4	4
<i>F</i> (000)	1064	1064
Collected reflections	7508	8011
Independent reflections	2501	2644

Parameters refined	145	145
GOF	1.022	1.067
$R_1$	0.0349	0.0401
$wR_2$	0.0854	0.1075

**Table S2.** Selected bond lengths [ $\text{\AA}$ ] for **1** at 213 K and 363 K.

Bond lengths	213 K	363 K
BI1—C11	2.6758(28)	2.6471(49)
BI1—C12	2.6167(17)	2.6217(22)
BI1—C13	2.5167(20)	2.5241(21)
BI1—C14	2.7256(29)	2.7221(50)
BI1—C15	2.8058(17)	2.8045(26)
Bi1—C15 <sup>i</sup>	3.0086(18)	2.9812(28)
C15—Bi1 <sup>ii</sup>	3.0086(18)	2.9812(28)
N1—C1	1.4574(103)	1.3963(132)
C1—S1	1.7963(137)	1.7743(184)
S1—C2	1.8167(95)	1.7549(109)
C2—C3	1.5070(138)	1.5037(222)
C3—N1	1.5059(161)	1.4220(249)
N2—C4	1.5026(112)	1.4397(165)
C4—S2	1.7786(138)	1.7708(257)
S2—C5	1.7934(122)	1.8450(151)
C5—C6	1.4917(185)	1.4090(276)
C6—N2	1.4715(217)	1.4632(278)

213 K: Symmetry codes: (i)  $-x+2, y+1/2, -z+1/2$ ; (ii)  $-x+2, y-1/2, -z+1/2$ .

363 K: Symmetry codes: (i)  $-x+1, y+1/2, -z+3/2$ ; (ii)  $-x+1, y-1/2, -z+3/2$ .

**Table S3.** Selected bond angles [ $^\circ$ ] for **1** at 213 K and 363 K.

Bond angles	213 K	363 K
-------------	-------	-------



Cl1—B11—Cl2	87.247(66)	89.810(91)
Cl1—B11—Cl3	92.239(74)	89.782(100)
Cl1—B11—Cl4	176.013(69)	176.447(115)
Cl1—B11—Cl5	92.522(66)	89.971(96)
Cl1—Bi1—Cl5 <sup>i</sup>	90.057(66)	90.197(102)
Cl2—B11—Cl3	93.910(66)	95.552(76)
Cl2—B11—Cl4	88.785(58)	88.991(29)
Cl2—B11—Cl5	179.741(50)	177.561(74)
Cl2—Bi1—Cl5 <sup>i</sup>	95.872(57)	93.024(75)
Cl3—B11—Cl4	87.704(69)	87.005(90)
Cl3—B11—Cl5	86.205(66)	86.876(79)
Cl3—Bi1—Cl5 <sup>i</sup>	170.049(68)	171.424(82)
Cl4—B11—Cl5	91.452(58)	91.368(85)
Cl4—Bi1—Cl5 <sup>i</sup>	90.676(62)	93.205(95)
Cl5—Bi1—Cl5 <sup>i</sup>	84.020(55)	84.548(81)
Bi1—Cl5—Bi1 <sup>ii</sup>	149.142(70)	154.225(106)
N1—C1—S1	106.622(608)	109.450(919)
C1—S1—C2	93.849(527)	95.735(683)
S1—C2—C3	106.159(622)	106.088(898)
C2—C3—N1	104.756(760)	113.988(1308)
C3—N1—C1	109.934(880)	114.629(1337)
N2—C4—S2	105.554(593)	106.844(1100)
C4—S2—C5	89.953(604)	91.078(936)
S2—C5—C6	107.375(937)	107.560(1291)
C5—C6—N2	109.398(1086)	113.065(1555)
C6—N2—C4	111.766(1031)	112.580(1489)

213 K: Symmetry codes: (i)  $-x+2, y+1/2, -z+1/2$ ; (ii)  $-x+2, y-1/2, -z+1/2$ .

363 K: Symmetry codes: (i)  $-x+1, y+1/2, -z+3/2$ ; (ii)  $-x+1, y-1/2, -z+3/2$ .

**Table S4.** Selected torsion angles [ $^{\circ}$ ] for **1** at 213 K and 363 K.

Bond angles	213 K	363 K
S1—C2—C3—N1	-37.0 (7)	-2.1 (13)
C1—N1—C3—C2	46.9 (8)	-0.2 (17)
C1—S1—C2—C3	16.6 (6)	2.9 (9)
C2—S1—C1—N1	9.5 (6)	-3.1 (10)
C3—N1—C1—S1	-33.9 (8)	2.3 (15)
S2—C5—C6—N2	24.3 (10)	9.9 (16)
C4—N2—C6—C5	2.2 (11)	11.3 (17)
C4—S2—C5—C6	-35.3 (8)	-21.9 (12)
C5—S2—C4—N2	35.7 (6)	27.8 (10)
C6—N2—C4—S2	-27.8 (9)	-27.5 (13)

**Table S5.** Hydrogen bonds under 213 K for **1**.

D—H···A	D—H	H···A	D···A	<DHA
N1—H1A···C15 <sup>viii</sup>	0.890	2.514	3.291	146.20
N1—H1B···C11 <sup>ix</sup>	0.890	2.373	3.247	167.01
N2—H2A···C12 <sup>iii</sup>	0.890	2.326	3.177	160.15
N2—H2B···C14 <sup>vi</sup>	0.890	2.280	3.158	168.90
C1—H1D···C13 <sup>viii</sup>	0.970	2.861	3.544	128.19
C3—H3A···C14 <sup>vii</sup>	0.970	2.812	3.755	164.40
C3—H3B···C11 <sup>viii</sup>	0.970	2.938	3.841	155.33
C4—H4A···C11 <sup>iv</sup>	0.970	2.782	3.588	141.71
C4—H4B···C14 <sup>iii</sup>	0.970	2.905	3.754	140.98
C5—H5A···S1 <sup>v</sup>	0.970	3.025	3.834	146.81

Symmetry codes: (iii)  $-x+1, y-1/2, -z+1/2$ ; (iv)  $x-1, y, z$ ; (v)  $x, y-1, z-1$ ; (vi)  $-x+1, y+1/2, -z+1/2$ ; (vii)  $x-1, -y+3/2, z+1/2$ ; (viii)  $-x+1, -y+1, -z+1$ ; (ix)  $-x+1, -y+2, -z+1$ .

**Table S6.** Hydrogen bonds under 363 K for **1**.

D—H···A	D—H	H···A	D···A	<DHA
---------	-----	-------	-------	------

N1—H1A···C13 <sup>v</sup>	0.890	2.958	3.606	131.05
N1—H1A···C15 <sup>v</sup>	0.890	2.723	3.350	128.48
N1—H1B···C12 <sup>iv</sup>	0.890	2.581	3.323	141.31
N2—H2A···C12	0.890	2.374	3.236	162.96
N2—H2B···C14 <sup>vi</sup>	0.890	2.410	3.283	166.54
C4—H4A···C11 <sup>i</sup>	0.970	2.840	3.588	134.49
C4—H4A···C15 <sup>vi</sup>	0.970	2.988	3.646	126.19
C4—H4B···C14	0.970	2.981	3.825	146.23

Symmetry codes: (i)  $-x+1, y+1/2, -z+3/2$ ; (iii)  $x+1, y, z$ ; (iv)  $-x+1, -y+1, -z+1$ ; (v)  $-x+1, -y, -z+1$ ; (vi)  $x, y+1, z$ .