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# Dielectric response and anhydrous proton conductivity in a chiral framework containing a non-polar molecular rotor

Shan-Shan Yu,[a] Shao-Xian Liu,[a] Hai-Bao Duan,*[a,b]

[a.]School of Environmental Science, Nanjing Xiaozhuang University, Nanjing 211171,, P.R.China

[b.]Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, United States

E-mail: duanhaibao4660@163.com

## 1. Experimental

### 1.1. Chemicals and reagents

Thee reagents and solvents were purchased from commercial sources and used without further purification.

### 1.2. Physical measurements

Elemental analyses (C, H and N) were performed with an Elementar Vario EL III analytical instrument. IR spectra were recorded on a Bruker Vector 22 Fourier Transform Infrared Spectrometer (170SX) (KBr disc). Thermogravimetric (TG) experiment was performed with a TA2000/2960 thermogravimetric analyzer from 30 to 600°C at a warming rate of 10 K/min under a nitrogen atmosphere, and the polycrystalline samples were placed in an aluminum crucible. Powder X-ray diffraction (PXRD) data for the as-prepared was collected using Bruker D8 Advance powder diffractometer operating at 40 kV and 40 mA with Cu K radiation $\lambda$ = 1.5418 Å at ambient temperature. Temperature and frequency dependent dielectric constant, $\varepsilon$', and dielectric loss, tan($\delta$), measurements were carried out employing Concept 80 system (Novocontrol, Germany); the powdered pellet, with a thickness of ca. 0.40 mm and 78.5 $mm^2$ in the area, was coated by gold films on the opposite surfaces and sandwiched by the copper electrodes and the ac frequencies span from 1 Hz to $10^6$ Hz.

**X-ray crystallography.** Selected crystals of **1** at room temperature were centered on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 3 CCD detector and a graphite monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å). The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis.[1] Structures were solved by the direct method and refined by the full-matrix least-squares procedure on $F^2$ using SHELXL-97 program.[2] The non-Hydrogen atoms were anisotropically refined using the full-matrix least-squares method on $F^2$. The crystallographic details about data collection, structural refinement and selected bond length and angle are summarized in Table 1 and 2.

### 1.3. Preparations for 1

The synthesis procedure of compound **1** is in following described: First, the $CoCl_2 \cdot 6H_2O$ (0.0237 g) and 1,4-diazabicyclo[2.2.2]octane (0.05 g) were dissolved in 6 ml DMF. The mixture were stirred for 3h, then 0.05 g phosphite was added and stirred another 1h. The mixture were sealed in Teflon-lined autoclave and heated to 60 ℃ for 72h. Blue needle-shape crystals were obtained in solution. The crystal was washed with DMF and acetone and dried in air. The yield is ca. 65% .

**References:**


1. *CrysAlis V1.171*, Oxford Diffraction Ltd., Poland, 2004.
2. G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal structure, University of Göttingen, Germany, 1997.


Table 1 Crystal and structural refinement data for compound **1**

| Complex | **1** |
|---|---|
| Molecular formula | $C_6H_{16}N_2CoP_2O_6$ |
| Molecular mass | 333.08 |
| Space group | $P2_12_12_1$ |
| Crystal system | orthorhombic |
| Temp/K | 296(2) |
| Wavelength (Å ) | 1.5406 |
| a/Å | 10.090(2) |
| b/Å | 10.782(5) |
| c/Å | 10.981(7) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| V/Å$^3$. Z | 1194.63(4) |
| μ/mm$^{-1}$ | 1.722 |
| λ/Å | 0.71073 |
| ρ/g cm$^{-3}$ | 1.85182 |
| F000 | 684 |
| $R_1$ | 0.0521 |
| $wR_2$ | 0.1240 |

Table 2 Selected Bond Lengths [Å] and Angles [deg] for compound **1**

| **1** | | | |
|---|---|---|---|
| Co(1)-O(4) | 1.934(4) | Co(1)-O(5) | 1.936(4) |
| Co(1)-O(3) | 1.957(4) | Co(1)-O(2A) | 1.961(4) |
| O(1)-P(1) | 1.524(4) | O(2)-P(1) | 1.505(4) |
| O(2)-Co(1B) | 1.961(4) | O(3)-P(1) | 1.512(4) |
| O(4)-Co(1)-O(5) | 109.63(18) | O(4)-Co(1)-O(3) | 110.44(16) |
| O(5)-Co(1)-O(3) | 102.13(18) | O(4)-Co(1)-O(2A) | 112.10(17) |
| O(5)-Co(1)-O(2A) | 111.94(18) | O(3)-Co(1)-O(2A) | 110.17(16) |
| P(2C)-O(4)-Co(1) | 130.2(2) | P(2)-O(5)-Co(1) | 148.1(3) |
| O(2)-P(1)-O(3) | 111.8(2) | O(2)-P(1)-O(1) | 113.5(2) |
| O(3)-P(1)-O(1) | 110.0(2) | O(2)-P(1)-H(3) | 106(3) |

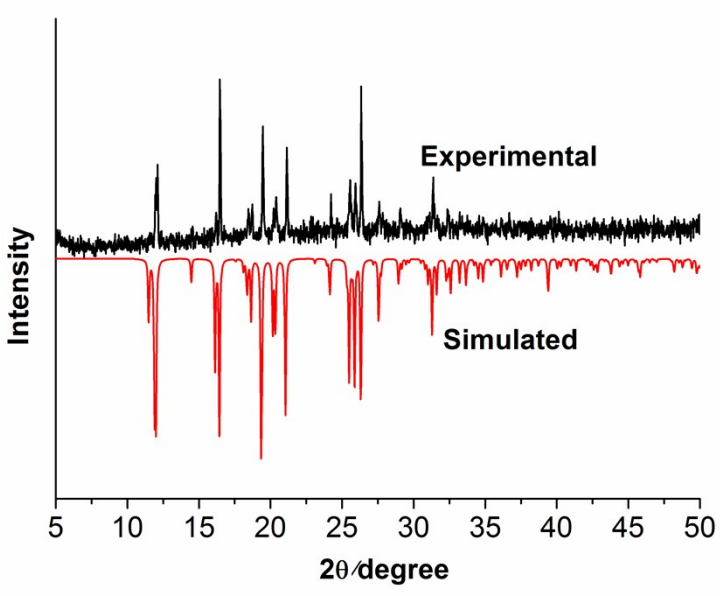


Figure S1 Powder X-ray diffraction patterns for as-prepared sample of **1**, confirming the phase purity of the as-prepared sample (Black lines: experimental patterns; red lines: simulated profiles).

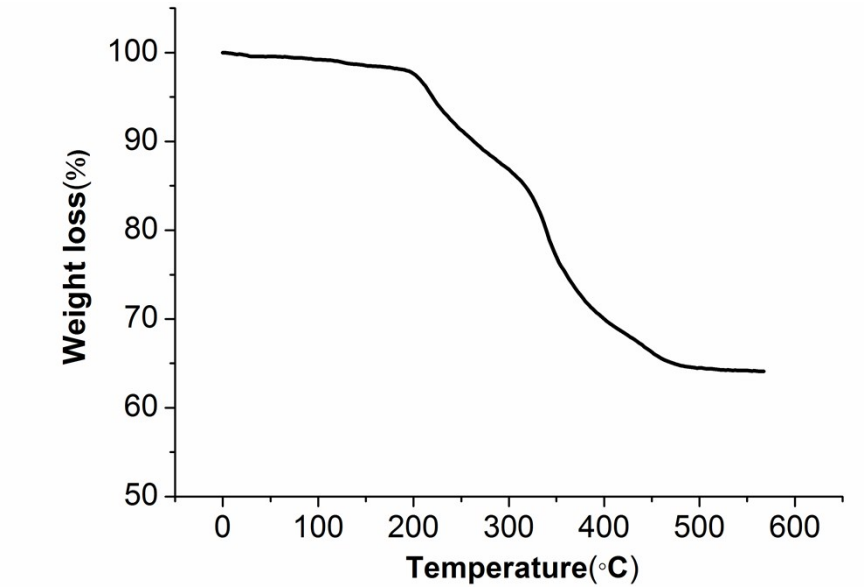


Figure S2 TG plot of **1** at selected temperature range

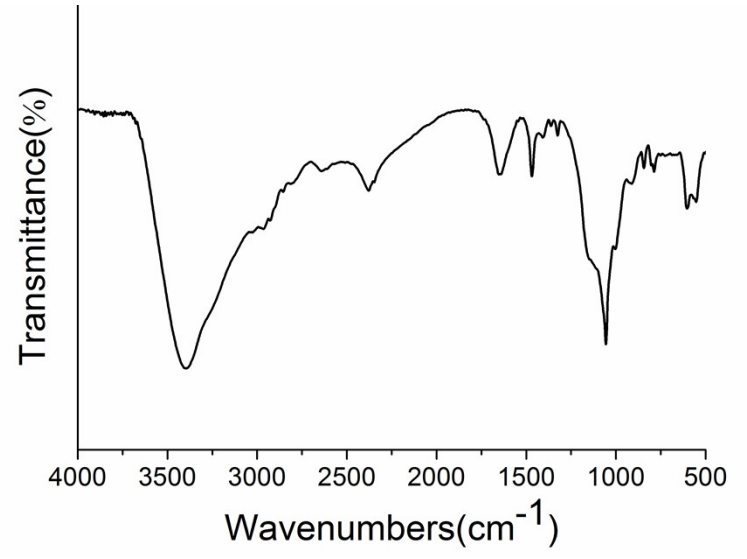


Figure S3 IR spectrum of **1** at room temperature

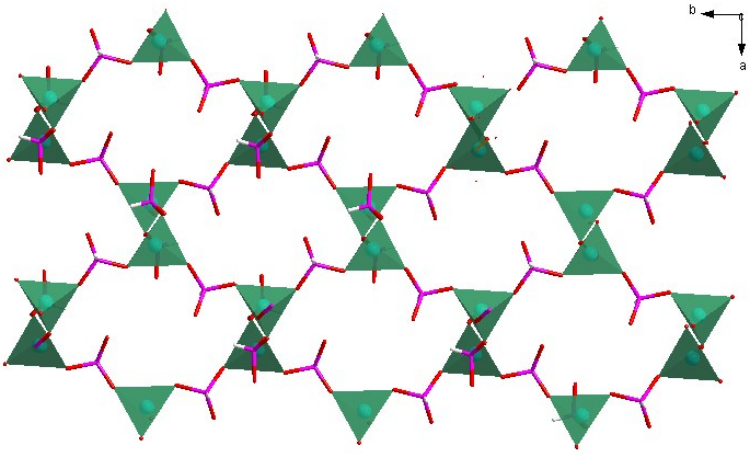


Figure S4 Crystal structure of **1** illustrating the 3D framework along the *c* axis

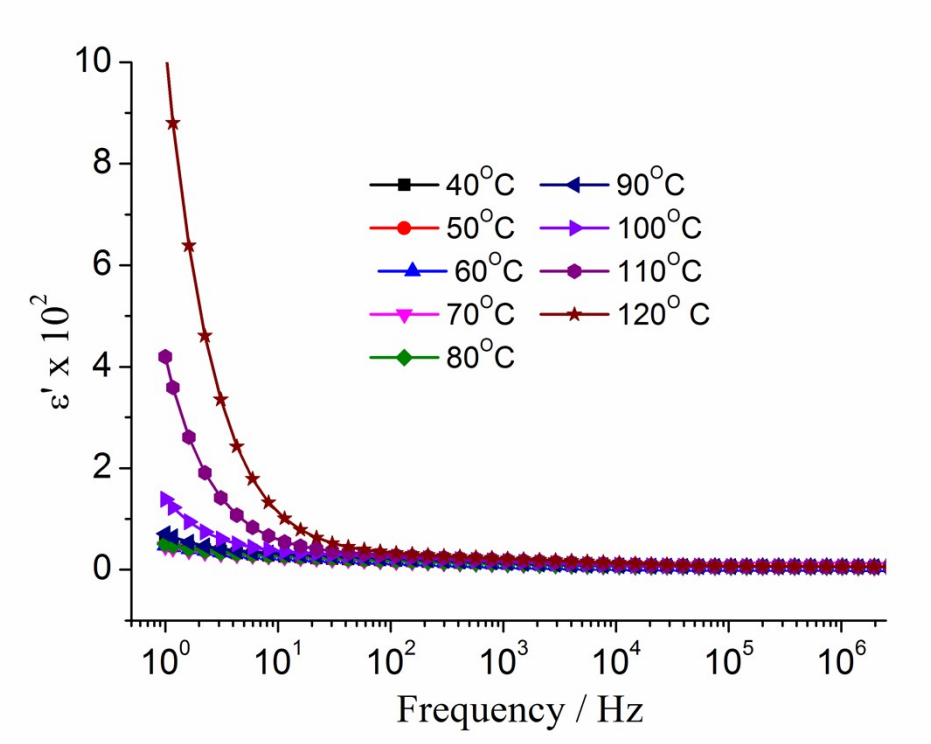


Figure S5 Frequency dependencies of the ε' of **1** in the 40-120 °C temperature range

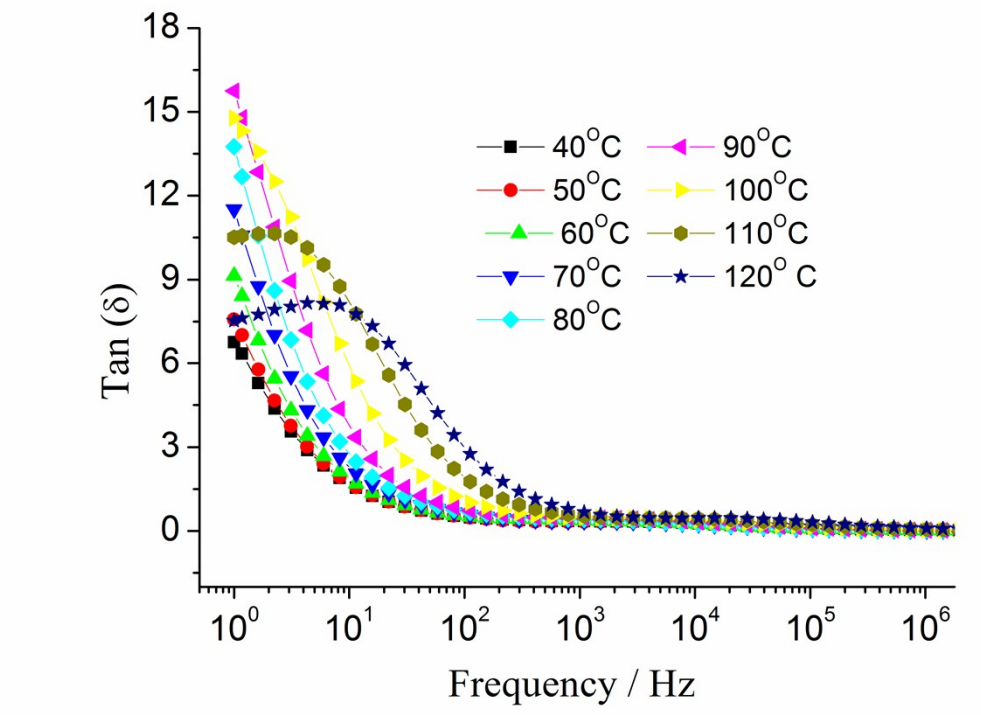


Figure S6 Frequency dependencies of *tan (δ)* of **1** in the 40-120 °C temperature range

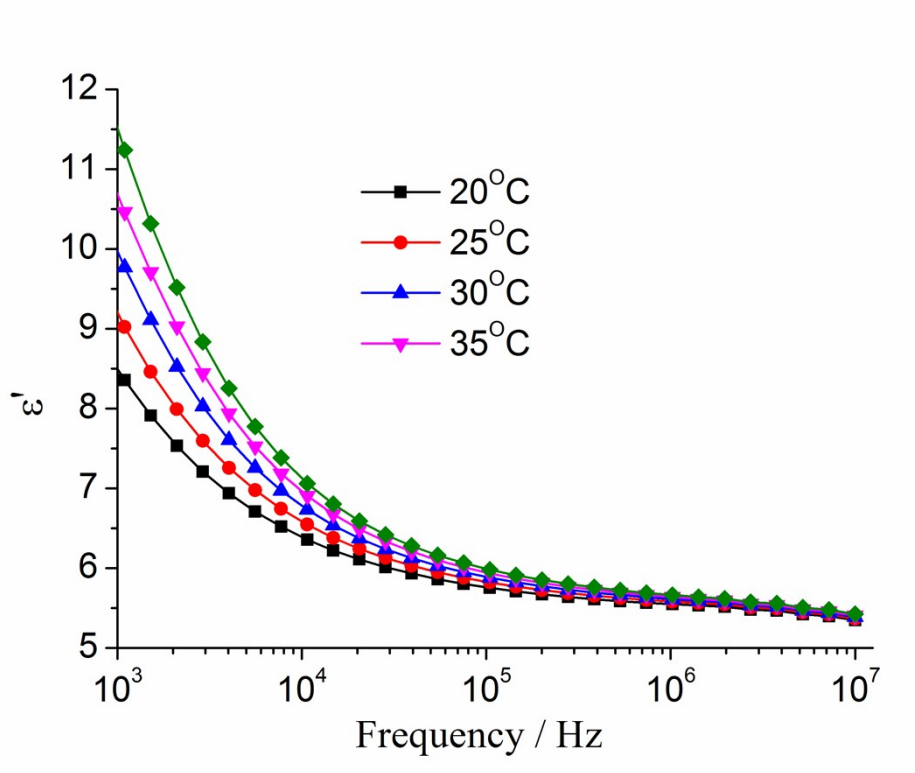


Figure S7 The ε' value of **1** in the room temperature range

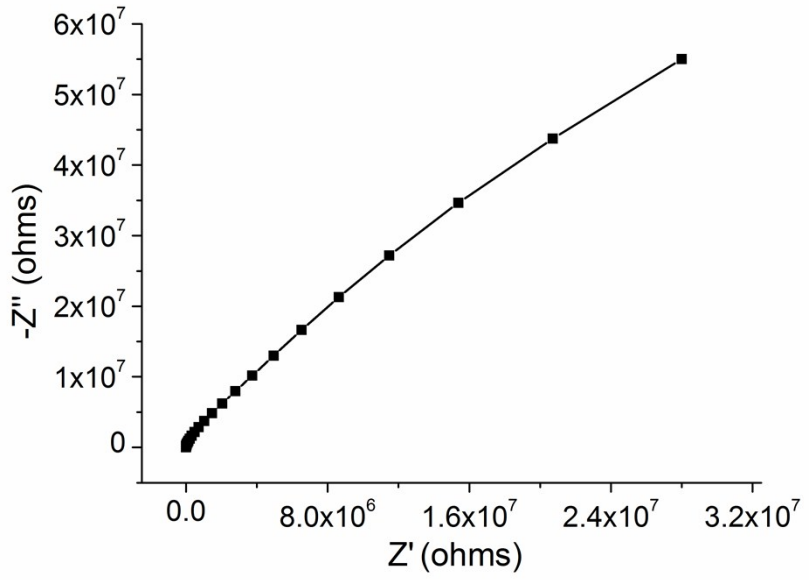


Figure S8 Complex impedance of **1** at 25 °C.