



Electric response in the antiferroelectric crystal of 4,4'-di-*t*-butyl-2,2'-bipyridyl with chloranilic acid

M. Rok*, A. Piecha-Bisiorek, P. Szklarz, G. Bator, L. Sobczyk

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

ARTICLE INFO

Article history:

Received 5 January 2015
In final form 26 February 2015
Available online 19 March 2015

Keywords:

Phase transition
Antiferroelectric
Supramolecular complex
Semiconducting

ABSTRACT

The electric response was analyzed in the vicinity of the structural phase transition at 412 K in the single crystals of 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone (chloranilic acid, CLA) with 4,4'-di-*t*-butyl-2,2'-bipyridyl (dtBBP). The dielectric permittivity of the complex measured along the *b* direction between 300 and 440 K and at frequencies ranging from 500 Hz to 2 MHz indicates two phenomena. At low frequencies, dielectric losses are ascribed to the electric conductivity of the crystal, while at high frequencies, to the dielectric relaxation described by means of the Cole–Cole relationship. The parameters of the dielectric response: the relaxation time, τ , the dielectric increment, $\epsilon_0 - \epsilon_\infty$, and the distribution parameter of the relaxation time, α , were estimated and analyzed. The low-temperature structure of the crystals indicates the antiferroelectric arrangement of the supramolecular hydrogen bonds. The dielectric results also presented for the deuterated crystals of dtBBP-CLA proved that the dynamics of protons in the hydrogen bonds are responsible for the mechanism of phase transition.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Proton transfer plays a crucial role in many chemical reactions or biological processes. Also, the proton dynamics in hydrogen bond determine a variety of interesting physical properties in crystals, like ferroelectricity [1–9], antiferroelectricity [10,11], protonic conductivity [12,13], and even semiconductivity [14–17]. Organic ferroelectrics with asymmetric hydrogen bonds, X–H···Y, have been intensively investigated as promising dielectric materials applicable in electronics [3,18,19]. In many recent reports, the results have been presented concerning the piezo-response force microscope (PFM) studies on organic systems, where ferroelectricity is induced by a cooperative intramolecular proton transfer [20–22]. An increased interest as regards these materials may be associated with: (i) the manner of their preparation – usually such functional materials can be obtained from the simple synthesis of two compounds from solution; (ii) the fact that they can be easily deposited and patterned by inject printing [23,24]; and (iii) the most important idea, that organic materials can be a good alternative to toxic inorganic oxides containing lead, bismuth, tantalum, or niobium. The investigations of the novel materials that exhibit a very large polarization value, which may be useful in capacitors and nonvolatile memories, have been discovered in systems of

benzoquinone acids with aromatic bases (e.g. pyridine and pyrazine derivatives). Benzoquinone-type compounds can be classified as intriguing compounds in supramolecular chemistry and crystal engineering. Their properties result from their molecular structure because their molecules possess two OH proton donor and two >C=O proton acceptor centers. From the intermolecular proton transfer viewpoint, the combination of complexes of halo-substituted derivatives of 3,6-dihydroxy-1,4-benzoquinones and bases having similar proton affinities guarantees the formation of agglomerates with a one-dimensional hydrogen bond as chains with a layer-type architecture. Crystals with these properties exhibit a strong anisotropy of physicochemical parameters. Likewise, complexes are named uniaxial ferroelectrics or one-dimensional conductors. In the case of long-range interactions, the proton dynamics can be estimated by the temperature measurement of the complex value of electric permittivity in the range of radio frequency.

The present paper is another contribution of ours concerning the electric properties of the organic supramolecular complex of 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone (chloranilic acid, CLA) with 4,4'-di-*t*-butyl-2,2'-bipyridyl (dtBBP) [25]. In the crystalline state, dtBBP forms hydrogen bonded chains with CLA. X-ray studies showed that chains of cations and anions, joined together by $N^+ - H \cdots O^-$ and $O - H \cdots O$ hydrogen bonds, were spread along the *b* axis. From one side of the CLA molecule, the proton transfer occurs. Furthermore, dtBBP molecules are arranged in a

* Corresponding author. Tel.: +48 71 375 72 88; fax: +48 71 328 23 48.

E-mail address: magdalena.rok@chem.uni.wroc.pl (M. Rok).

π - π stacking. DSC measurements show a weak, close-to-continuous, phase transition at 412/410 K (on heating/cooling). The complex dielectric permittivity for a single crystal sample was measured, but the parameters of the dielectric relaxation were not estimated.

The problem undertaken in this paper is related to the determination of the parameters of the electric response of dtBBP-CLA in the vicinity of phase transition at 412 K in order to explain its mechanism. At first look, the mechanism of the transition seems to be quite simple: it is related to the proton jumps along the chain of the OHN hydrogen bridges. We would like to estimate the parameters of the potential for the proton motion in the hydrogen bond and through the measurements of the deuterated sample to prove that the mechanism is really connected with the proton/deuterium dynamics. The problem seems to be interesting from the viewpoint of crystal engineering, with bipyridyl and chloranilic acids as components, linked *via* the chains of hydrogen bonds.

2. Experiment

2.1. Preparation

The complex of chloranilic acid (CLA) (Aldrich, >98%) with 4,4'-di-*t*-butyl-2,2'-bipyridyl (dtBBP) (Aldrich, >98%) (1:1) was prepared by a diffusion method in acetone. Single crystals were grown from the acetonitrile solution (Fig. 1).

The deuteration of CLA was performed by stirring the chloranilic acid solution with CH₃OD (Aldrich, >99%) for 20 h. The stirring cycle was repeated three times. The degree of deuteration was monitored by the infrared vibrational spectra of the KBr disk (Fig. 2). From the IR spectra, two characteristic bands were used: (i) ν (OH) at 3238 cm⁻¹ and ν (OD) at 2418 cm⁻¹; (ii) γ (OD) at 693 cm⁻¹ and γ (OD) at 503 cm⁻¹. The ratio of integral intensities was estimated in the case of ν OH/OD to be 63% and in the case of γ OH/OD to be *circa* 80%. The average value of the deuteration degree was 72%. The obtained acid was used in the preparation of complexes, from the dtBBP solution in acetonitrile with 10% of CH₃OD. The full description of the INS, IR, and Raman spectroscopy of non-deuterated and deuterated chloranilic acid was presented by Pawlukojć et al. [26]

2.2. Dielectric properties

The complex admittance, $Y = G + i\omega C$, was measured using an Agilent 4284A Precision LCR Meter in the frequency range between 500 Hz and 2 MHz and in the temperature range between 300 and 440 K. The single crystal samples were crystallographically oriented and measured along different directions. The



Fig. 1. Single crystals of the dtBBP-CLA complex crystallized from acetonitrile solution.

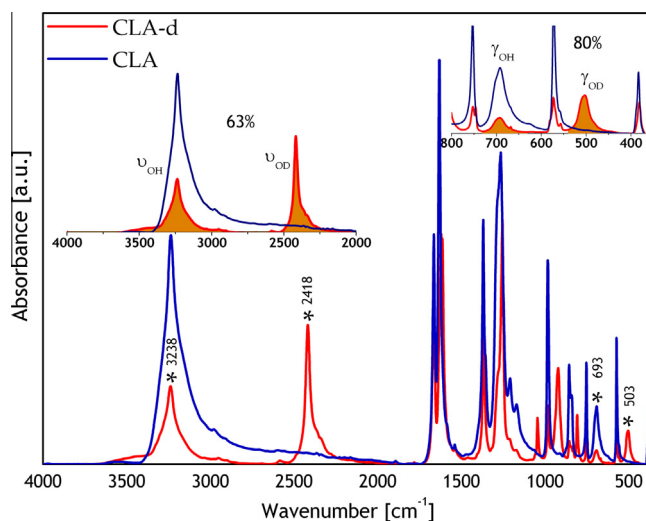


Fig. 2. Comparison of IR spectra for non-deuterated and deuterated chloranilic acid in a KBr disk.

measurements along the *b* axis, where the largest value of the permittivity was observed, were performed on a 5 × 3 × 1 mm [3] sample. During the experiment, two types of electrodes were used: (i) copper-foil electrodes affixed to the prepared crystals; (ii) silver-painted sample plates. The overall error in the estimation of the real part of the complex dielectric permittivity value was less than 5% and that of conductivity was 10%.

2.3. DC conductivity

The *dc* conductivity was measured along the *b* direction with a Keithley 6517D electrometer in the temperature range between 300 and 440 K.

3. Results and discussion

The main purpose of this work was to carry out the electric measurements of dtBBP-CLA single crystals as a function of temperature and frequency. The measurements were scrutinized on cooling and heating, and the corresponding runs are reversible. Fig. 3 presents the dielectric response measured along different

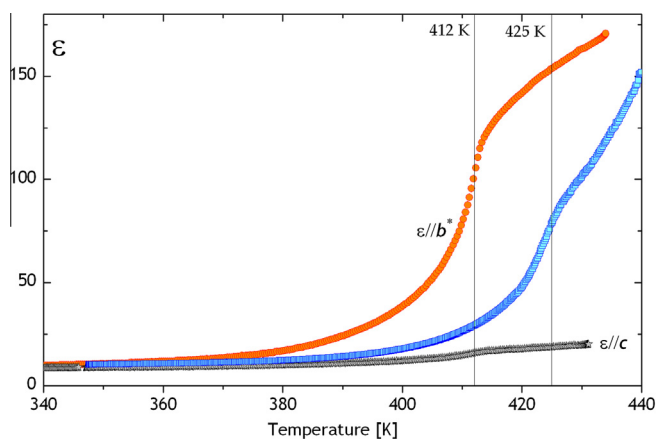


Fig. 3. The temperature dependence of relative permittivity measured with the *ac* field at the frequency of 1 kHz. The dielectric response of a deuterated complex (72%) is presented by blue squares. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/5373267>

Download Persian Version:

<https://daneshyari.com/article/5373267>

[Daneshyari.com](https://daneshyari.com)