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High dielectric constant response of modified copper phthalocyanine

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ABSTRACT

The dielectric properties of copper phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid tetrasodium salt (CuPc_TS) and copper phthalocyanine octacarboxylic acid (CuPc*) were investigated from 20 Hz to 1 MHz with relative humidity from 0 to 75%. A dielectric constant $>10^6$ was found at 1 kHz and 20% humidity for the modified copper phthalocyanines. Humidity increases the dielectric constant, which is attributed to increasing ionization of the peripheral groups as the water enters into the samples.

1. Introduction

Since 1948 when Eley discovered the semiconducting property of phthalocyanines (Pc's) [1], these compounds have become one of the most investigated organic semiconductors [2] due to their high chemical stability and electrical properties. They have found applications in fuel cells [3–5], organic photovoltaics [6–8], organic field effect transistors (as a gate dielectric) [9,10], and humidity and chemical sensors [11,12]. Pc's electronic and optical properties can be tuned by substituting the central metal atom, the peripheral group or by adding dopants. Metal phthalocyanines (MePcs) can have a wide variety of metal atoms at the center of the molecule. One of the most widely studied MePcs is copper phthalocyanine (CuPc), shown in Fig. 1a. The CuPc molecule does not have a dipole moment because of its symmetry; however the large delocalization of the π-electrons within the phthalocyanine ring leads to a high electronic polarizability of 1.2×10^{-22} cm^3, which enhances the dielectric constant [13]. Nalwa et al. reported a very high dielectric constant $>10^5$ at 1 kHz and 120 °C for what was assumed to be a tetrameric copper phthalocyanine in 1986 [13]. Mezei et al. [14] used mass spectrometric analysis to show that what had been proposed to be a "tetramer" or "oligomer" is actually monomeric CuPc*. Nalwa's work led to several applications, including electro-active polymers for actuators (so-called artificial muscles) and micro-fluidic systems for drug delivery [15–17]. Zhang et al. [18] and Saha and Mandal [19] discussed the materials' use as a filler in a polymer matrix for all-organic composite actuator materials. Opris et al. [21] reported a high dielectric constant associated with monomeric octacarboxylic CuPc, formed from dipentyl-4,5-dicyanophthalate. The dielectric constant value was $>10^3$ at frequencies less than 10^4 Hz.

The exact reason for the high dielectric constant remains uncertain. Several factors have been suggested [17,20] to cause the effect. Relevant factors include water uptake [21], oxygen exposure [22], treatment with different solvents [13], and the relative orientation of Pc molecules when exposed to an external electric field [23–25]. Lunkenheimer et al. [26] have shown that external factors can produce high apparent values of the dielectric constant in inorganic semiconductors. An explanation for a polyacene quinone radical polymer based on phenothiazine and metallic tri-anhydride, where the dielectric constant reached ~1800 at 1 kHz, was given based on hyper-electronic polarization by Pohl and Hartman et al. [27].

In this article we report a colossal dielectric response for the modified CuPc materials CuPc* (Fig. 1b) and CuPc_TS (Fig. 1c) and the results are compared with standard CuPc. CuPc_TS is water soluble due to the sulfonic acid group on its periphery, making it interesting for applications using solution processing. CuPc_TS has been tested for organic photovoltaic devices [28–30], is used as a dye [31,32], and is an antiviral drug (against HIV) [33].

2. Background

The electric polarization P of a molecule is induced by the electric field in non-polar materials but is permanent in polar molecules. There are several microscopic mechanisms for polarization in dielectric materials which depend on the frequency of the electric field [34]. The first polarization mechanism is the electronic polarization P_e, which describes the displacement of the cloud of bound electrons with respect to the nucleus under an applied electric field. Electronic polarization is present in all atoms and exists up to ~10^{15} Hz. The second type is

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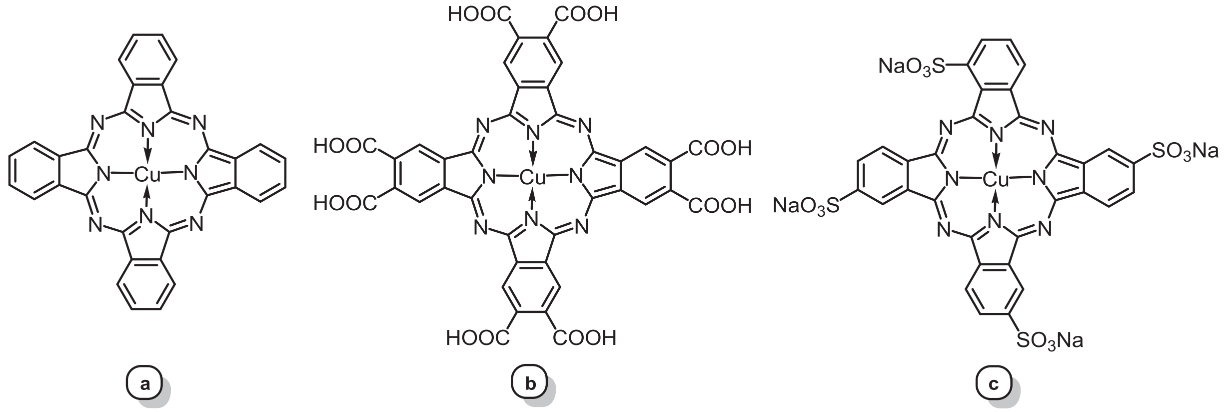

Fig. 1. Structure of a) standard CuPc, b) copper phthalocyanine octacarboxylic acid (CuPc*) and c) copper phthalocyanine 3, 4′, 4″, 4‴-tetrasulfonic acid tetrasodium salt (CuPc_TS).

ionic polarization P_i which relates to the stretching or compressing of a bond by the electric field, which changes the dipole moment of the molecule. It can be operative up to infrared frequencies (~10^{13} Hz). Ionic polarization is present in materials made of different kinds of ions due to the sharing of the valence electrons. Since the response times for electronic and ionic polarizations are very short, they are considered together as an induced dipole moment [35,36].

The third type is orientational polarization P_o (dipole polarization) which is found in dipolar materials which have an asymmetrical structure where randomly oriented permanent dipoles occur in the absence of a field. When an external field is present they align with the field. This kind of polarization exists in gases, liquids, and polymeric materials. As the temperature increases, the thermal energy of molecules increases, reducing the importance of internal molecular forces [37], and making it easier to align the dipoles with the electric field. It is typically active up to the microwave frequencies (10^8 Hz) and its temperature dependence follows the Debye equation [35,36]

$$P = N\frac{2\mu_0{}^2}{3kT}E \tag{1}$$

where k is Boltzmann's constant, T is the temperature in Kelvin, μ_0 is the permanent dipole moment, N is the number of molecules per m^3, and E is the applied electric field. Generally, orientational polarization is much larger than electronic or ionic polarization, and it can be easily discerned by the temperature dependence of the dielectric constant.

The fourth type of polarization is interfacial or space charge polarization P_i, which arises from local charge accumulation. It often occurs at boundaries and interphase surfaces. P_i typically contributes to the polarization up to ~10^4 Hz. A number of dielectric materials have very high dielectric constants at lower frequencies due to interfacial polarization [22,35,38]. Another polarization mechanism was suggested by Pohl and Hartman et al. [27] and is called hyper-electronic polarization P_h. It has been found in long polymeric molecules which have an extensive region of electronic orbital delocalization; due to interaction between pairs of excitons, it is active up to ~10^6 Hz [39]. The total polarization can be approximated by:

$$P = P_e + P_i + P_o + P_{sc} + P_h. \tag{2}$$

This equation ignores interactions between different polarization mechanisms, which will generally be a higher order effect. A spontaneous polarization would also need to be added for a ferroelectric material.

3. Experimental

Standard CuPc pellets were made from ground single crystals grown by sublimation. Copper phthalocyanine-3, 4′, 4″, 4‴-tetrasulfonic acid tetrasodium salt (85%) was purchased from Sigma-Aldrich and used as received. We synthesized CuPc* following the method described by Poole and Owens with a modification of the copper source, that is, using $CuSO_4 \cdot 5H_2O$ instead of $CuCl_2$ [40]. Samples were pressed into 12 mm diameter disks ~1 mm thick at a pressure of ~55 MPa using a hydraulic press. The copper electrodes had the same diameter as the pellet.

Thin films of CuPc_TS were tested by sandwiching the material between two electrodes, with an indium-tin oxide (ITO) coated slide as the lower contact. The ITO was cleaned in an ultrasonic cleaner; acetone, iso-propanol and distilled water were used in subsequent rinses of 15 min each. Finally a UV-Ozone cleaner (BioForce-Nanosciences) was used for 30 min to remove organic residues from the ITO surface and achieve good wetting between the ITO and the solution. A CuPc_TS solution (0.02 M) was stirred for a week, filtered using 0.45 μm filter paper, then spin-coated on the ITO at 300 rpm for 20 s then 1000 rpm for 60 s using a Chemat Technology KW-4A spin coater. Thickness and morphology were determined using an atomic force microscope (AFM) from ThermoMicroscopes Auto Probes. Finally, 100 nm of thermally evaporated silver provided the upper contact.

The complex linear dielectric constant is given by $\varepsilon^*(\omega) = \varepsilon' - i\varepsilon''$ where ε' and ε'' are the dielectric constant and the dielectric loss, and $\tan\delta = \varepsilon''/\varepsilon'$. We measured capacitance from 20 Hz to 1 MHz using a QuadTech 1920 capacitance meter. The signal amplitude was 1 V. The dielectric constant was determined using

$$\varepsilon' = \frac{C\,d}{\varepsilon_0\,A} \tag{3}$$

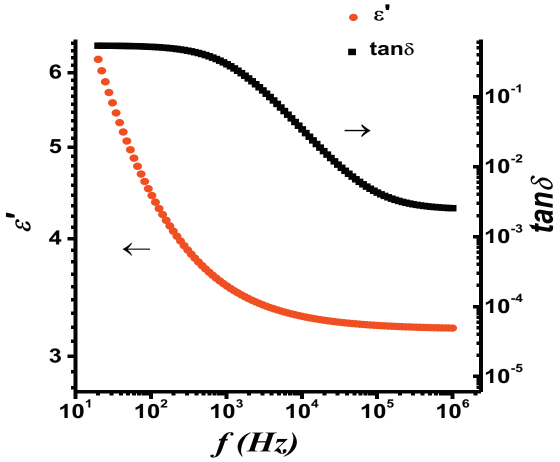

Fig. 2. Dielectric constant and dielectric loss tangent at room temperature and 20% RH for standard CuPc.